DOCUMENT RESUME

ED 052 938 SE 010 844

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TITLE Automobile Engine Development, Task Force Assessment, Preliminary Report.
PUB DATE 30 Jun 70
NOTE 87p.

EDRS PRICE EDRS Price MF-$0.65 HC-$3.29
DESCRIPTORS *Air Pollution Control, *Engines, *Environmental Influences, Fuels, *Motor Vehicles, Pollution, Projects, Reports, Research
IDENTIFIERS Project Clean Air

ABSTRACT

This report presents a comprehensive survey of current knowledge and ongoing research and development projects in the area of vehicular emissions and control. Information provided attempts to answer the questions: how can proposed standards be met with existing technology and what additional research would be required to obtain desired control effectively and economically? The survey covers basic pollutant formation processes, emission characteristics of conventional and non-conventional engines, current and proposed control techniques, alternative power plants, special problems of chemical analysis of vehicle emissions, and effects of fuels and additives. Although no specific projects are recommended for Project Clean Air, the areas of Catalysis, Basic Combustion, Conventional Engine Development, Non-Conventional Engines, and Battery Development are proposed as basic study areas. The report was prepared by one of seven special task forces studying various air pollution problems, particularly in California, with the aim of making tentative recommendations as to what the University of California can do through Project Clean Air to alleviate these problems. (BL)

ED052938

PROJECT CLEAN AIR

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TASK FORCE NO. 1

AUTOMOBILE ENGINE DEVELOPMENT

TASK FORCE ASSESSMENT

Preliminary Report

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For

The Executive Director
of
Project Clean Air

U N I V E R S I T Y O F C A L I F O R N I A

June 30, 1970

SE 010 844

FOREWORD

This preliminary report was prepared by one of the seven special Task Forces of Project Clean Air. Prepared for the Executive Director of Project Clean Air, this and the related preliminary reports from the other six Task Forces summarize assessments of the state of knowledge on various air pollution problems, particularly in California, and make tentative recommendations as to what the University of California can do through Project Clean Air to alleviate those problems. The Task Forces and their air pollution assessment areas are as follows:

Task Force No. 1	Automobile Engine Development
Task Force No. 2	Human Health Effects
Task Force No. 3	Social Sciences
Task Force No. 4	Meteorology and Simulation Models
Task Force No. 5	Power, Industry, Agriculture, and Ecology
Task Force No. 6	Instrumentation Development
Task Force No. 7	Atmospheric Chemistry and Physics

Task Force No. 1 Members

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ABSTRACT

This report presents a comprehensive survey of current knowledge and ongoing research and development projects in the area of vehicular emissions and control. The survey covers fundamental processes, conventional and non-conventional engines, chemical analysis of vehicle emissions, and fuel and additive effects. Although no specific projects are recommended for Project Clean Air, the areas of Catalysis, Basic Combustion, Conventional Engine Development, Non-Conventional Engines, and Battery Development are proposed as basic study areas. Projects within these areas have been suggested on the basis of faculty interest.

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Section 1

INTRODUCTION AND SUMMARY

1.1 NATURE OF THE REPORT

This report was primarily intended to give a review of the current knowledge and ongoing research and development efforts in the area of automotive emissions and control. The overall air pollution problem is a complex one whose solution will require the interaction of various disciplines. It is not the purpose of this report, however, to examine these interactions. Rather, we take the premise that controls will be set for automotive emissions on the basis of health, economic, or social considerations. The information provided here attempts to answer the questions: how can any proposed standards be met with existing technology? And what additional research would be required to obtain desired control effectively and economically?

1.2 OVERALL PLAN

The main section of the report is devoted to the review of existing technology. Included in this section are discussions of basic pollutant formation processes, emissions characteristics of current engines, current and proposed control techniques, alternative power plants, special problems of chemical analysis, and effects of fuels and additives. This information has been gathered by literature review and correspondence with various university, private, and governmental research organizations concerned with the problems of vehicle emissions and control. This main review section provides the basis for the subsequent information on research requirements and projects recommended for Project Clean Air.

1.3 RECOMMENDATIONS

No specific research projects are recommended. Five general subject areas have been recommended for Project Clean Air Research. These are: Catalysis, Basic Combustion Studies, Conventional Engine Development, Non-Conventional Engines, and Battery Systems. Specific projects have been suggested in each subject area. These topics, based on an expressed faculty interest, are given below.

The target date for initial application of results from this research is set as 1974-1975. This late date was set because of indications that there is a tremendous research effort currently ongoing in the automobile industry to meet emissions standards currently enacted in California for 1971-1974.

1.3.1 Catalysis

The most economical means to meet future emissions standards may be the use of catalytic control devices. Existing prototype control devices usually require expensive catalysts which must be replaced fairly often. The development of effective catalytic devices will require fundamental study of the physics and chemistry of the catalyst reactions and development of effective catalysts for control of pollutants. A necessary adjunct to this will be the design and testing of control devices in actual vehicle service.

1.3.2 Basic Combustion

Studies of basic combustion processes, both in current engines and combustors typical of proposed power plants can lead to techniques for pollution control in the engine itself. In addition the study of chemical reactions under conditions typical of homogeneous exhaust reactors can lead to better understanding of the design of such devices. The following research topics have been proposed: chemistry of combustion reactions, combustion modeling in engines, droplet burning studies, and experimental work on engine combustion.

1.3.3 Conventional Vehicle Development

This is the area where the greatest amount of research is being done by private industry. One of the main problems requiring study here is the emissions of aldehydes. These compounds which are important in photochemical smog production are not measured in typical exhaust analyses. It has also been proposed that an extensive vehicle testing lab be set up as part of Project Clean Air. Once established this lab could be used to study immediate problems as they arise. A study of the use of cryogenic oxygen in engines to eliminate nitrogen oxide emissions has also been proposed.

1.3.4 Non-Conventional Vehicles

This area perhaps warrants more attention by Project Clean Air than studies of conventional vehicles as it is important to reconcile various claims of cost and practicality for use of a different basic power plant. Work on steam car development, design and testing of combustors for non-conventional engines, and the construction of a hybrid heat engine/electric vehicle have been proposed.

1.3.5 Battery Development

Two faculty members have expressed an interest in the development of batteries with the necessary energy and power densities for vehicular applications. It is recommended also that consideration be given to the overall change in pollution caused by the introduction of electric vehicles which obtain electricity from another pollution source-electric power plants.

Section 2

STATE OF THE ART

2.1 OVERALL PLAN

This section will present a discussion of the present knowledge in vehicle emissions and control. It will cover basic engine combustion as related to pollutant production, currently available control techniques, and proposed systems for future reduction of emissions. The first, and major, part will be devoted to a discussion of the currently used spark-ignition, reciptrocating-piston internal combustion engine. This will be followed by a discussion of diesel engines, gas turbines, external combustion engines, electric vehicles, and hybrid propulsion systems. Finally general discussions of vehicle emissions measurements and effects of fuels and additives will be given.

2.2 EMISSIONS FROM MOTOR VEHICLES

The automobile is the main source of three atmospheric pollutants: carbon monoxide, hydrocarbons and nitrogen oxides. Although it contributes relatively small amounts of sulfur oxides and particulates, it is a major source of particulate lead. The relative importance of automotive air pollution varies with geographical location and time of year. In terms of total mass the automobile plays a dominant role in air pollution, contributing 60% of the total mass of pollutants nationwide, 88% in Los Angeles, and 71% in the San Francisco Bay Area. These statistics are somewhat misleading since the major pollutant from the automobile, on a mass basis, is carbon monoxide. From a health standpoint, this compound is one of the least noxious emissions; this is indicated by the California air quality standard of 20 ppm CO. This is a higher allowed concentration than that of other common pollutants.

The automobile is still responsible, nationwide and especially in California, for the largest share of hydrocarbon and nitrogen oxides emissions. These, of course, are the compounds responsible for the formation of photochemical smog. Control of emissions from automobiles is then aimed at three basic pollutants: carbon monoxide, hydrocarbons, and nitrogen oxides. The controls of particulate lead emissions from vehicles has also been discussed and will be considered below.

The uncontrolled automobile has three major sources of emissions: the exhaust, the crankcase blowby, and the fuel tank and carburetor evaporation. All the carbon monoxide and nitrogen

oxides emissions and 55% of the hydrocarbon emissions come from the exhaust pipe. The remaining hydrocarbon emissions come 25% from the crankcase and 20% from evaporation. In passing legislation for control of exhaust emissions it is necessary to specify some typical driving cycle to test the various operating conditions of the vehicle. The first driving cycle was developed in the Los Angeles area in the mid 1950s and is the so-called "California cycle." This cycle consists of idle, acceleration, cruise, and deceleration modes. A major criticism of this cycle is that it has no high speed cruise operation which would be representative of freeway driving. Nevertheless this driving cycle is the basic standard test on which all emissions legislation is based.

Although the initial exhaust emissions standards were in terms of concentrations, recent laws have been passed in terms of a mass emission standard. Data on past, present and proposed legislation are presented in Table I.

Table I. Mass Emissions Standards (Gm/Mi.)

	Prior to Control	1966 Calif. 1968 Fed.	Calif. AB 357 (1967)				Proposed Standards 1975		1980
			1970	1971	1972	1974	Calif.	Fed.	Fed.
Hydrocarbons	11.0	3.4	2.2	2.2	1.5	1.5	0.5	0.45	0.25
Carbon monoxide	80.0	34.0	23.0	23.0	23.0	23.0	12.0	11.0	6.0
Nitrogen oxides	4.0	--	--	4.0	3.0	1.3	1.0	0.9	0.5

The proposed 1975 California standards have been enacted by the State Air Resources Board, but have not yet received the necessary approval from the Secretary of Health, Education and Welfare. The proposed federal standards for 1975 are stricter than California's and if these are enacted into law they would supercede the state standards.

Controls on crankcase blowby have been installed on cars since 1962. These consist essentially of returning the blowby gas to the engine rather than venting it to the atmosphere. Evaporative emissions controls were required on all 1970 model year vehicles sold in California. These controls typically use some adsorbent such as activated charcoal which adsorbs the evaporative emissions while the vehicle is stopped. Air is passed through those devices when the vehicle is restarted to desorb the hydrocarbons and feed them to the engine.

It can be seen from Table I that the legislated and proposed standards are becoming increasingly more stringent. The current approach to emissions control has been the modification of existing reciprocating, spark-ignition, Otto cycle engines. It may become economically sound to go to some other type of engine to meet the lower emissions standards proposed for the future, since the types of controls required on current engines will become more and more expensive to meet these standards.

The automobile manufacturer is concerned with the overall product. Thus for any new control system or vehicle concept one has to consider normal vehicle performance requirements. These include not only fuel economy and power output, but also such nebulous concepts as driveability. (The last is a term used to describe the general impression the driver has about the performance of the car. Some control systems will cause surging or incipient engine stalling and are said to give poor driveability.) The decision of which vehicle systems are appropriate to meet all demands of performance and pollution must be based on a careful analysis of all available control techniques and alternative powerplants.

2.3 FORMATION OF POLLUTANTS IN SPARK-IGNITION ENGINES

2.3.1 Basic Engine Combustion Processes

Because of their practical importance combustion processes have been studied for many years. The basic nature of a combustion process for energy production involves the subsonic passage of a flame front (deflagration) through a combustible mixture. (This can be as a spatial motion of the front through a quiescent mixture or a flow of reactants into a stationary flame.) The passage of this front depends on a feedback of energy and species to maintain the reaction. It is also possible to have low temperature oxidation processes which are not associated with a flame, but these processes are generally much slower than the reactions in the flame front. Although the quantitative reaction rate is a strong function of the actual combustor geometry the basic nature of the combustion process, the passage of the flame front, is an essential feature of all combustors.

Edwards and Teague (1970) have discussed the application of basic combustion theory to an understanding of spark-ignition engine phenomena. In the ordinary engine the flame front passes across the combustion chamber while the piston is near the top of the cylinder. Direct photographic observations have shown that the flame is highly turbulent due to mixture motion in the cylinder. The typical time scale for passage of the flame across the cylinder is about 5 msec. This process is repeated every 25-100 msec. Because the piston is decelerating, coming to a stop, and

accelerating in the opposite direction during this time, the combustion takes place at nearly constant volume. Thus many of the ideas of constant volume combustion can be applied to a qualitative understanding of engine combustion.

In constant volume combustion, the passage of a flame causes the burned gases to expand, compressing the unburned bases. When the final mass is consumed, the expansion of the last mass to burn recompresses the first mass to burn. In this compression-expansion process the first mass to burn does work $P_{initial}\ \Delta V$ at the start of combustion and receives work $P_{final}\ \Delta V$ at the end of the process. Since the final pressure is greater than the initial pressure the net effect of the expansion/compression is to add the energy $(P_{final} - P_{initial})\ \Delta V$ to the first mass to burn. Similarly the last mass to burn loses energy in this process. The net effect is the setting up of a temperature gradient across the volume. This temperature difference can amount to a few hundred degrees Kelvin. The temperatures in the burned gases will be about 2,500-3,000°K, at the end of the combustion process.

At these temperatures virtually all of the hydrocarbons in the bulk gas will be consumed. The flame cannot propagate completely to the cylinder wall, however, since this wall is cooled externally and is at a relatively low temperature (ca 500°K). Thus the mixture in the region of the wall does not react. Consequently, hydrocarbons and oxygen present in this region will be exhausted.

During the power stroke the gases rapidly expand. Here the temperature drops at a rate of about 70-90° K/msec, strongly decreasing the rates of chemical reactions. The exhaust valve is opened near the end of the power stroke and gases flow into the exhaust system. Typical exhaust temperatures immediately after the exhaust valve are 1000-1300°K. It is thus possible to have some reaction in the exhaust line, before the gases enter the atmosphere.

There are many parameters that can be studied with respect to engine operation. The most important ones are equivalence ratio*, spark timing, load or power output**, speed, compression

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* Equivalence ratio is defined as $\frac{(fuel/air)_{actual}}{(fuel/air)_{stoichiometric}}$, and given the symbol ϕ. Thus ϕ equal to, less than, or greater than 1 denotes a fuel/air mixture which is chemically correct, fuel lean, or fuel rich, respectively.

** For given engine speed the load increases as the inlet manifold pressure increases; for this reason manifold pressure is often used as a measure of engine load.

ratio, and surface/volume ratio in the combustion chamber. The last two are obviously functions of the engine design. The first 4 are functions of the engine operating conditions. In order to determine the approach for controlling emissions it is important to know the effects of these various engine parameters on the production of the various pollutants.

2.3.2 Exhaust Hydrocarbons

There have been several papers studying the effects of engine operations on the production of exhaust hydrocarbons (e.g., Jackson, et al., 1964, Hagen and Holiday, 1964). A large amount of work in the field of exhaust hydrocarbon emissions has been done by W. A. Daniel and his co-workers at General Motors. In a series of papers, (Daniel, 1956, Daniel and Wentworth, 1964, Wentworth and Daniel, 1964, Daniel, 1968, Daniel, 1970) they have examined the causes for production of hydrocarbons in engine exhaust. The main thesis of the work is that the hydrocarbons are mainly produced by the quenching of the flame at the cold cylinder walls. That is, the bulk cylinder gases do not contain any significant amount of hydrocarbons.

There are two sources for hydrocarbons: (1) the walls of the open part of the combustion chamber, and (2) the "crevices"--parts of the engine cylinder separated from the main combustion chamber by restrictive passages. Hydrocarbons that are produced by flame quenching can flow (or diffuse) away from the wall and be further oxidized after flame passage; preferential exhausting of burned products can exist, and finally further oxidation of hydrocarbons can take place in the exhaust system. Daniel (1970) examined the effects of equivalence ratio, compression ratio, engine speed, ignition timing, air flow on the causes of hydrocarbon emissions. (Note that this choice of independent variables means that the engine load is determined by the air flow rate.) Using an analysis which involved many assumptions he obtained the following interpretation of the experimental data.

Decreasing the equivalence ratio (i.e., increasing the air/fuel ratio) decreased the exhaust hydrocarbon concentration as a result of decreases in the unburned material in the crevices and an increase in the fraction of the hydrocarbons which underwent further oxidation in the combustion chamber and exhaust system. There is an optimum equivalence ratio, usually 0.8 - 0.9, for minimizing exhaust hydrocarbons. Operation at leaner equivalence ratios tends to produce more hydrocarbons. This may be due to poor ignition in these leaner mixtures.

Decreasing the air-flow rate decreased the hydrocarbon concentration as a result of decreases in unburned fuel left in both the crevices and the main chamber. In addition the fraction of unburned hydrocarbons exhausted decreased. The degree of oxidation

of the hydrocarbons decreased but this was not significant.

Decreasing the compression ratio decreased the hydrocarbon emissions by changing all factors to favor lower hydrocarbon emissions except the degree of oxidation of quench hydrocarbons which was not changed.

The exhaust hydrocarbon concentrations were decreased when the engine speed was increased due to decreases in the amount of unburned material in the main chamber and the crevices. In addition the degree of oxidation both in the combustion chamber and in the exhaust system increased. All these effects were sufficient to overcome the increase in the fraction of unburned hydrocarbons entering the exhaust system.

The ignition timing could be retarded (i.e., the combustion process started later in the compression stroke) to decrease hydrocarbon concentration. This was a result of decreasing unburned fuel in the crevices and increasing the fraction oxidized in the exhaust system as the spark comes closer to the end of the compression.

In summary, it appears that the concentration differences observed when engine variables were changed were due largely to changes in the amount of hydrocarbons produced in the crevices. The exception to this was that the major changes in hydrocarbon concentrations when ignition timing was changed were due to increases in the fraction of hydrocarbons oxidized in the exhaust. In general, quenching in the open chamber walls and crevices were about equally important in determining the production of exhaust hydrocarbons. On the average about one-third of the hydrocarbons left at the end of the combustion process ultimately entered the atmosphere. Of the rest about one-third were oxidized in the combustion chamber after the flame passage, and only half of the hydrocarbons in the cylinder were exhausted. Finally about 10% of the exhausted hydrocarbons were oxidized in the exhaust system.

2.3.3 Exhaust Reactivity

Although all the discussion so far has not considered specific hydrocarbons it is important to note that not all hydrocarbons are equally effective in the production of photochemical smog. The ability of a given hydrocarbon to produce smog is called its reactivity. There are many different measures that have been proposed for hydrocarbon reactivity (Altshuler, 1966; Maga and Kinosian, 1968; Caplan, 1968; Jackson, 1968). These include the oxident formation rate, the hydrocarbon consumption rate, the NO_2 consumption rate, biological effects and product yields and so forth. Altshuler (1966) shows that on various scales the qualitative increases in reactivity can be described by the following order of increasing reactivity:

- C_1-C_5 paraffins, acetylene, benzene
- C_6+ paraffins
- toluene and other monoalkylbenzene
- ethylene
- dialkyl and trialkylbenzenes
- 1-alkenes
- internally bonded alkenes

The quantitative values assigned to various compounds vary widely, however. The values based on reaction rates can vary by factors of 100 or more; values based on eye irritation can be fit on a scale of 0-3 (Heuss and Glasson, 1968). The California State Department of Public Health has proposed a simple yes-no system where hydrocarbons are classified as either reactive or non-reactive (Maga and Kinosian, 1968). This is equivalent to using a weighting factor of zero (non-reactive) or one (reactive). The reactive/non-reactive rating essentially rates any hydrocarbon that forms any smog product as reactive. Methane, ethane, propane, butanes, pentanes, acetylene, and benzene were considered non-reactive. Maga and Kinosian have listed several proposed reactivity scales. They have pointed out the discrepancies caused by the varying scales by showing that the carburetor evaporative emissions were calculated to be 1.7, 1.0, or 0.8 times as reactive as exhaust hydrocarbons based on three different reactivity scales.

Jackson (1968) has studied the effects of engine operating conditions on exhaust reactivity. He found that the increase in reactivity caused by richer mixtures was less than the increase in hydrocarbon concentration. This is easily explained by the fact that the richer mixtures tended to produce higher amounts of non-reactive compounds. (The fraction of the total hydrocarbons due to non-reactive methane and acetylene increased from 4% to 43% as the mixture was richened.) Jackson also found that retarded spark timing tended to reduce the exhaust hydrocarbon concentrations but increased the exhaust reactivity.

One of the major difficulties in considerations of exhaust reactivity is the chemical analysis involved. Current techniques generally require a complete chromatographic analysis of all the hydrocarbons in the exhaust. The time involved in such an analysis makes it virtually unfeasible for routine work. Certainly the concept of reactivity is a useful one in assessing the real smog effects of hydrocarbon emissions, but it will be necessary to find a simpler means of analysis and an appropriate reactivity scale before this measure can be used in setting legal emissions standards.

2.3.4 Carbon Monoxide

The formation of carbon monoxide in combustion processes is mainly due to an insufficient amount of oxygen for complete conversion to CO_2. The only variable which has any significant effect on exhaust CO concentrations is the equivalence ratio (Hagen and Holiday, 1964; Huls, et al., 1968). Other engine variables alter CO concentration through changes in equivalence ratio.

In the combustion of hydrocarbons the only reaction considered to be important in the production of CO_2 is

$$CO + OH = CO_2 + H$$

Consequently all carbon atoms, in the initial hydrocarbon fuel, exist at one point in the combustion process in the form of carbon monoxide. It is well known from basic thermodynamics that the equilibrium concentration of CO increases with temperature for a given atomic composition and pressure. Consequently at the end of the combustion process in the engine there can be large concentrations of carbon monoxide present due to two possible effects: 1) nonequilibrium in the combustion reactions leading to large concentrations of the intermediate CO, and 2) high equilibrium concentrations of carbon monoxide due to high temperatures at the end of combustion.

In either case, the final exhaust concentrations of carbon monoxide are determined by the chemical kinetic processes taking place in the expansion. Newhall (1969) has shown, by numerical integration of the chemical kinetics that the reaction $CO + OH = CO_2 + H$ is so fast that it can be assumed to be at all times in a state of partial equilibrium. That is, the mole ratio n_{CO}/n_{CO_2} is given by the following equation

$$\frac{n_{CO}}{n_{CO_2}} = \frac{1}{K} \frac{n_H}{n_{OH}}$$

where K is the equilibrium constant. This equation holds even when the overall chemical system is out of equilibrium. Thus the CO/CO_2 ratio is determined by the H/OH ratio in the expansion gases. The concentrations of the latter species are determined by the relatively slow recombination reactions

$$H + H + M = H_2 + M$$

$$H + OH + M = H_2O + M$$

These reactions tend to produce an H/OH ratio that is higher than equilibrium. Consequently the CO concentration is higher than that predicted by equilibrium for the exhaust temperature.

Control of carbon monoxide emissions lies in operation of the engines at leaner equivalence ratios so as to produce less CO or subsequent oxidation of carbon monoxide in the exhaust system. To reach very low levels of CO , a combination of the two will probably be required.

2.3.5 Oxides of Nitrogen

The formation of nitrogen oxides in combustion processes is one of the best understood and quantitatively predictable steps. There are many reasons for this. Basic kinetic studies of the nitrogen oxides have been made for many years because the slow reaction rates of these species allowed kinetic measurements with relatively slow response equipment. In addition the emphasis of the nation's space program on the reentry problem necessitated an accurate understanding and quantitative measurement of the kinetics of nitrogen/oxygen systems.

The effects of engine operating parameters on nitrogen oxides have been studied by many people including Gilbert, et al. (1957), Nebel and Jackson (1958), Wimmer and McReynolds (1961) and Huls and Nickol (1967). It was generally found that engine equivalence ratio played a major role in determining concentrations of nitrogen oxides in engine exhausts. The concentration of nitrogen oxides is a maximum at a slightly lean equivalence ratio (ca. ϕ = 0.95). Also, at a given equivalence ratio it was found that nitrogen oxides increased as peak temperatures increased. Thus a change in any engine parameter, e.g., compression ratio, spark advance, intake pressure, which would increase peak temperatures was found to increase nitrogen oxide production in the exhaust. Under conditions existing in ordinary spark ignition engines, thermodynamic equilibrium calculations indicate that the only significant oxide of nitrogen that should be present is nitric oxide, NO . Mass spectrometric measurements by Campau and Neerman (1967) showed that this was indeed the case. In all cases they studied, the total nitrogen oxide concentration in the exhaust (NO_x) always contained at least 98% NO with the remainder being NO_2 . Thus, for purposes of analyzing nitrogen oxide formation in spark ignition engines, it is sufficient to consider NO as the only significant oxide of nitrogen.

In initial studies on nitrogen oxide production it was found that the exhaust nitric oxide concentrations could be roughly predicted by calculating the equilibrium nitric oxide concentration at peak cycle temperature. (This is actually an assumed temperature calculated by measuring the pressure during the cycle, calculating the charge mass from the fuel and air flow rates and the engine

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speed, assuming an appropriate molecular weight for the burned gases, and using the ideal gas law. Such an analysis ignores the existence of gradients in temperature and concentration in the engine cylinder.) As a result of this fact it was concluded that the nitric oxide is formed during the combustion process and its concentration is frozen. To check this, Newhall and Starkman (1967) analyzed the concentration of nitric oxide during the expansion process by observing the infrared emission from the combustion gases through a window in the combustion chamber of an operating engine. They showed that there was no change in the NO mole fraction during the expansion process indicating that the NO concentration was indeed frozen. These experimental results confirmed a simplified kinetic analysis of the nitric oxide decomposition process. Newhall (1969) subsequently performed a detailed kinetic analysis of the expansion process investigating the reactions of the nonhydrocarbon species. These detailed calculations also showed no nitric oxide decomposition during the expansion process.

The kinetics of the nitrogen oxide system are usually described by the following elementary reactions (Lavoie, et al., 1970).

$$N + O_2 = NO + O \quad (1)$$

$$O + N_2 = NO + N \quad (2)$$

$$N + OH = NO + H \quad (3)$$

$$H + N_2O = N_2 + OH \quad (4)$$

$$O + N_2O = N_2 + O_2 \quad (5)$$

$$O + N_2O = NO + NO \quad (6)$$

$$N + O + M = NO + M \quad (7)$$

$$N_2 + O + M = N_2O + M \quad (8)$$

The first two steps form the Zeldovich (1946) mechanism. This mechanism is generally sufficient to account for the NO formation under conditions present in spark ignition engines (Newhall and Starkman, 1967, Newhall and Shahed, 1970, Lavoie, et al., 1970). The mechanism involving N_2O becomes important at lower temperatures (about 2000°K). The mechanism given by equations 5 and 6 can appear to be a direct bimolecular reaction of $N_2 + O_2 = NO + NO$ since reaction 5 is much faster than reaction 6. Although the earlier literature on NO kinetics invoked this "direct bimolecular

step" it is generally disregarded today. The final three elementary reactions play a very minor role and are generally disregarded.

One of the important features of the Zeldovich mechanism in combustion processes is that the O + N_2 reaction can be started by oxygen atoms produced as free radicals in the combustion process. Thus, it is not correct to analyze the NO kinetics separately from the combustion process since the presence of these O atoms must be taken into account.

Eyzat and Guibet (1967, 1968) performed a simplified kinetic analysis of the formation of NO during the combustion process. Although they were able to obtain agreement between predictions and measurements their kinetic analysis was open to question since it assumed the direct bimolecular reaction and extrapolated rate data taken at temperatures below 1700°K to temperatures of 3000°K. Two recent studies on nitric oxide formation in combustion processes are described below.

Lavoie et al. (1970) used an L-head single cylinder (CFR) engine in which the flame passage could be observed at different intervals. Here the nitric oxide concentration was measured as a function of time. This study also took into account the temperature gradients caused by the flame passage across the cylinder. They showed that the formation kinetics of NO were important in determining the final concentration and they also showed that there was a substantial temperature and, hence, nitric oxide gradient in the combustion chamber.

Newhall and Shahed (1970) studied NO formation in a high pressure cylinder initially charged with a fuel air mixture and ignited by a set of spark plugs on one end of the cylinder. A nearly flat flame then passed along the length of the cylinder past a window used to measure the concentration optically. Their results showed that in lean mixtures there was a significant departure from chemical equilibrium in the burned gases. The typical data observed for nitric oxide formation in engines can easily be interpreted as being near equilibrium in the rich region and kinetically limited in the lean region. Since the equilibrium NO concentrations in the rich region are relatively small the fact that these concentrations are in equilibrium and not kinetically limited is not so important.

In summary, nitric oxide concentrations in engines are strongly influenced by equivalence ratio and temperature. The equivalence is usually fixed by the requirements for consistent ignition and flame propagation. For a given, fixed, equivalence ratio any process which reduces the temperature can reduce the nitric oxide mole fraction. Among the processes suggested, to do this have been retarded spark advance, decreased compression ratio, addition of inserts to the fuel-air charge (e.g. water insection and exhaust gas recycle and the use

of gaseous fuels which allow operation at very lean conditions. The efficacy these various suggested control techniques is discussed below. The practical aspects of these ideas and their implication on overall engine performance and production of other pollutants will be considered.

2.3.6. Oxygenated and Polynuclear Aromatic Hydrocarbons

These compounds are usually given special attention but the amount of information available about emission of these compounds from engines is sparse. The oxygenated hydrocarbons, aldehydes and ketones, play a role in the photochemical smog process. If these compounds are photochemical intermediates formed slowly in the atmosphere the engine can act as a promoter of the smog process by introducing them directly into the atmosphere. In addition, formaldehyde which is the dominant oxygenated hydrocarbon in vehicle exhaust is not detected by usual hydrocarbon analyses. Thus control techniques which may only partially oxidize hydrocarbons to formaldehyde may actually be making smog worse even though an improvement is indicated. The polynuclear aromatic hydrocarbons are important since they are known to be carcinogenic to the skin of animals and humans.

Because of difficulties in chemical analysis there is a lack of detailed studies on the emissions of oxygenates and the effects of engine variables on their production. The main work in this area appears to be that of Oberdorfer (1967). His work indicated that ketones comprise a small fraction of oxygenated hydrocarbons. Consequently the terms oxygenates, carbonyls and total aldehydes are used interchangeably. Oberdorfer also found that, of the total aldehydes (and ketones) on a composite driving cycle, 70.2 mole percent were formaldehyde. In most tests on vehicles a gravemetric technique was used in which the carbonyl compounds were reacted with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazone derivatives which were precipitated out and weighed. All additional mass was presumed to be formaldehyde. The concentration of aldehydes in the exhaust deduced from this technique will be higher than the actual concentration, but the error should be reasonable since such a large amount is actually formaldehyde.

Oberdorfer found that cars with no exhaust controls produced about 100 to 280 ppm of aldehydes on the California cycle. The aldehyde level increased, in general, when total hydrocarbons were lower. Cars with exhaust emissions controls exhibited a similar level of aldehydes, even though the level of unburned hydrocarbons was lower. Adehyde levels decreased from cars with control devices when levels of other hydrocarbons decrease. The most important variable affecting aldehyde concentrations in exhaust was the equivalence ratio.

It appears as if there are significant levels of aldehydes in automotive exhaust gas. Unfortunately official measurement techniques

do not give a good measure of these compounds which are important in the formation of photochemical smog. As allowable levels of hydrocarbons become lower it will be necessary to obtain a good measure of the exhaust aldehydes for enforcement and control.

The relationship between air pollution and lung diseases such as lung cancer has often been questioned. A study at Sloan-Kettering Institute for Cancer Research (Wynder and Hammond, 1962, Hoffman and Wynder, 1962) found that automobile exhaust "tar" had about twice the carcinogenic activity of tobacco smoke condensate in terms of skin tumors in mice. The concentrations of known carcinogenic compounds found in the automotive "tar" are 50 to 100 times greater than their concentrations in the tobacco smoke condensate. The compounds rated most active by Hoffman and Wynder are benzo(a)pyrene and dibenz(a,h)anthracene. The authors point out that there is, of course, a great difference between cigarette smoke components which are inhaled directly into human lungs and the "tar" from automobile exhausts which would be greatly diluted before being breathed. Further, an analysis of epidemiological evidence concluded that the differences in incidence of lung cancer (nearly twofold greater in urban areas) could not be attributed conclusively to air pollution because of the possibility of other differences between urban and rural life patterns. Despite this inconclusive result special attention has been given to the polynuclear aromatic compounds in automotive exhaust because of the possibility of unknown carcinogenic effects in humans.

The work at Sloan-Kettering was a collaborative effort with work at General Motors Research (Begeman, 1964, Colucci and Begeman, 1965). Begeman found that the production of "tar" was about 1 gram per kilogram of fuel for a "modern 8-cylinder engine" running on commercial gasoline over a driving cycle. In analyses of individual components in this tar it was found that benzo(a)pyrene was present at a concentration of 32 ppm, giving an emission rate of 240 micrograms of benzo(a)pyrene per 1000 $ft.^3$ of exhaust gas.

It was found that fuel composition had a significant effect on "tar" production. In addition to the experiments run with commercial gasoline the following other fuels were used: isooctane (2,2,4-trimethylpentane), diisobutylene (2,2,4-trimethyl-3-pentene), and a 50:50 mixture of benzene and o-xylene. The total amount of "tar" produced was 0.49, 0.50, 2.4, and 1.7 gm./1000 $ft.^3$ of exhaust gas for diisobutylene, isooctane, gasoline, and the benzene/o-xylene mixture, respectively. The emissions of benzo(a)pyrene from these fuels (in the same order) were 18, 64,240 and 646 µgm./1000 $ft.^3$ of exhaust gas. Thus the aromatic fuel gave a sharp increase in the amount of the benzo(a)pyrene.

The paper by Colucci and Begeman describes measurements on the concentration of "tar" and specific components of that "tar" in the

atmosphere. It was found that the contribution of the automobile to the overall atmospheric concentration varied greatly with geographic location, even in a single large city. The automotive contribution to "tar" varied from 14-31% and its contribution to benzo(a)pyrene varied from 5-42%.

No specific plans for control of polynuclear aromatic hydrocarbons appear to be formulated. The concentration of benzo(a)pyrene in the exhaust can be reduced by lowering aromatic content of gasoline.

2.4 CONTROL TECHNIQUES

2.4.1 CO and HC Emission Control Using Engine Modifications

The results of the engine modifications made from 1961 to 1970 show an 80% reduction in hydrocarbons from all sources and a 70% reduction in carbon monoxide during that period (Heinen, 1969). The initial reduction of pollutants was by easily installed crankcase ventilation controls. The procedure for controlling crankcase emissions was by closing the crankcase vent and recycling the crankcase gases back through the combustion process. These controls, introduced in 1962, essentially eliminated the 25% of the hydrocarbon emissions coming from the crankcase blowby. 1970 model year cars have evaporative emissions control systems. Although these systems are new the claim of 80% reduction of hydrocarbon emissions is based on the assumption that these devices achieve nearly complete elimination of evaporative hydrocarbons. The control of crankcase blowby is generally considered to be solved and is not discussed further in this report. Control of evaporative emissions is discussed below in Section 2.4.3.

In 1966 for compliance with California standards for exhaust hydrocarbon and CO emissions, various systems were developed by the Detroit manufacturers. Ford and General Motors used a combination of a leaner air-fuel mixture and an air injection into the exhaust manifold (Chandler, et al., 1968, Steinhagen et al., 1968). The Chrysler Clean Air Package utilized a leaner air-fuel mixture, retarded timing at idle, and advance timing during deceleration (Beckman et al., 1968). In 1968 and 1969 Ford and General Motors abandoned their air injection pump and adopted a control system similar to Chrysler's. The objection to a leaner air-fuel mixture is while HC and CO emissions are reduced, oxides of nitrogen are increased. Further engine modifications to lower hydrocarbons and CO are reduced compression ratios, redesign of combustion chambers, heated intake air, single plane intake manifolds, and modified carburetors.

Stratified charge engines (Bishop and Simco, 1968) in which the fuel is not mixed with the air but is injected directly into the

combustion chamber just before combustion have been proposed for reduction of hydrocarbon and CO emissions. These engines have long been recognized as having good fuel economy and fair torque and power characteristics in addition to relatively low emissions. Stratified charge engines are hampered, however, by their increased complexity, reduced power output for a given engine size, and high production costs.

Although significant reduction of hydrocarbon and CO emissions have been obtained to date by relatively simple engine modifications it appears that future standards cannot be met by extension of these techniques. In addition, when nitric oxide controls become effective, it is necessary to consider the design of a total emission control system since some techniques which are effective for control of CO and hydrocarbons in engines (e.g. leaner fuel/air mixtures) can increase nitrogen oxides. Thus future control techniques will probably involve some sort of exhaust reactor, either homogeneous or catalytic.

2.4.2 Homogeneous Exhaust Reactors

One method of controlling the levels of carbon monoxide and unburned hydrocarbons which are emitted by internal combustion engines is to provide an environment outside the cylinders that will promote further oxidation of the exhaust combustibles. Studies by DePont and Esso researchers show that homogeneous exhaust reactors are a feasible solution to lowering carbon monoxide and hydrocarbon emissions.

Over the past five years studies undertaken by Cantwell and coworkers at Du Pont (1965, 1969, 1970) have resulted in the development of a series of reactors which effectively reduce exhaust emissions. Design considerations noted by Cantwell and Pahnke dealt with the conservation of thermal energy, the provision for sufficient volume and mixing, and problems encountered in the installation of the system. Emission levels of .25 grams of hydrocarbons and 5.0 grams of carbon monoxide per mile have been achieved with good driveability, little loss in fuel economy (1 to 1.5 miles per gallon), and satisfactory vehicle performance. The reactors are compatible with systems for controlling evaporative losses and with exhaust gas recirculation for control of nitric oxides.

An air injection system developed by Glass, Kim, and Kraus (1970) effectively reduces carbon monoxide and hydrocarbon emissions. Since reactor efficiency requires a fuel rich mixture, air injection is mandatory. The Esso researchers have developed an injection system which synchronizes the air injection with the individual exhaust valve openings. Using a Du Pont reactor they obtained hydrocarbon emissions of .125 grams per mile. This is a significant reduction from the non-synchronized version. The

synchronizer system includes a presently available air pump and a chopper type synchronizer run at 1/2 crank speed.

Erosion tests on the reactor cores showed that CrAl diffusion coatings, Al dipping and plasma-jet sprayed 80Ni20Al coating, all prevent oxidation to a large extent. There is a program now underway to develop economically feasible metals which can withstand the high temperatures associated with the reactor core. Further simplifications in reactor design coupled with cheaper alloys will contribute to a lower ultimate cost per unit.

A mathematical model for determining reactor volumes necessary for combustible oxidation has been developed by Schwing (1970). In using this model, the reactor is simulated by a continuously stirred tank in which mixing is assumed to be perfect. Schwing obtained the appropriate empirical constants to allow this model to be used for design of these reactors. One of us(PDV) has used this model in the successful design of a reactor for a 1970 Plymouth. This car is entered in the Clean Air Car Race, a nationwide low-pollution-vehicle design contest for university students.

Although the coupling of homogeneous exhaust reactors to some vehicles pose definite problems due to lack of room or engine configuration their application over the next few years or as a permanent solution seems entirely feasible.

2.4.3 Evaporative Emissions and Control

The evaporative emissions from automotive fuel systems (fuel tank and carburetor) are the most recent source of hydrocarbons to be controlled. As mentioned previously these controls started with 1970 model year cars in California.

Jackson and Everett (1969) and Ebersole (1969) have studied the reactivity of evaporative emissions. The effect of fuel composition on the amount and reactivity of evaporative emissions is significant. Evaporative emission reactivity per gram increases with increasing C_4 and C_5 olefins in the fuel and decreases with increasing C_4 and C_5 paraffins. Jackson and Everett (1969) from General Motors developed an equation (the Evaporative Reactive Index, ERI) which is the product of amount and reactivity per gram and is a good measure of the contribution of evaporative emissions to photochemical air pollution. This empirical equation is able to predict changes in ERI corresponding to variances in fuel composition or volatility for cars with no evaporative controls. Ebersole (1969) developed a method for determining hydrocarbon reactivities that accounts for nonlinear relations between reactivities and mixture concentration. A mathematical model for prediction of carburetor and fuel tank losses has been developed by Koell (1969).

The method most common and very effective in controlling evaporative emissions is the adsorption-regeneration approach. Systems utilizing this principle have been developed and are used on 1970 model-year vehicles in this state. The concept of the system is based on controlled adsorption-desorption cycling. Hydrocarbon vapors, which would normally be lost to the atmosphere, are adsorbed, stored and fed during purging, into the intake system. Neither exhaust emissions nor engine operation are altered by this approach.

The heart of the evaporative loss control device (ELCD) is the charcoal canister which adsorbs hydrocarbons from the carburetor and fuel tank during the hot soak condition and the diurnal cycle and is purged under a predetermined exhaust manifold backpressure condition, during subsequent engine operation. Appropriate valving is provided to accomplish the cycle.

Extensive studies on the development of this specific type of activated carbon have been done by Joyce et al. (1969). They have resulted in a product which is long-lived, dependable and maintenance-free, compact and simple, adaptable to all cars, and should approach total and absolute solution to the problem.

Although the problem of measuring evaporative emissions is an intricate one, Martens and Thruston (1968) have designed, built and tested a Sealed Housing for Evaporative Determinations (SHED). This provides an accurate method for the determination of these emissions. The legal standard is 6 grams per test. Current control systems generally do much better than this standard.

Evaporative emissions from automobiles can be significantly lowered by reducing gasoline volatility without using any control devices. A slight reduction in the Reid vapor pressure can lower evaporative losses over 50%. A survey by Nelson (1969) of the Los Angeles area showed that lowering the volatility of gasolines could be accomplished without sacrificing driveability and still contribute to a reduction in hydrocarbon emission.

Nevertheless, Wilson et al. (1968) say that the reduction of fuel volatility to 5-6 psig Reid vapor pressure for areas of low temperature (50°F and lower) might be expected to result in lowering warm-up performance of a large number of cars in the hands of the general public.

The adsorption systems appear to offer nearly complete control of evaporative emissions. There is the possibility, however, that some improvements can be achieved in reducing evaporative emissions from pre-1970 cars by modification of fuel composition.

2.4.4 Control of Nitrogen Oxides (Noncatalytic)

As mentioned in the previous section on nitrogen oxides the means of control of this pollutant are based on reduction of peak temperatures and on the time spent at high temperatures. The time/temperature pattern can be altered by changing the ignition timing. This will give some reduction in NO emissions and allows cars to meet the 1971 California standards. For future standards this technique will be used in conjunction with some other control technique. Because the homogeneous decomposition rates of NO are so slow no homogeneous exhaust treatment process is possible to reduce the levels of this compound once it is formed. The NO must be prevented from forming or removed catalytically in the exhaust.

One of the proposed techniques for reduction of the NO formation is the use of charge dilution to reduce the temperatures in the engine. This can be done by water injection or exhaust gas recirculation. Of these two, exhaust gas recirculation seems to be the better choice since it does not require an auxiliary water tank.

Glass et al. (1970) reported that exhaust gas recirculation could reduce the levels of NO in the exhaust by 60% for cars equipped with either air injection or other engine modifications. The exhaust flow required to do this was about 12.5% of the air flow rate to the engine. They also showed that simple disconnection of the vacuum spark advance would reduce NO by about 45% with about a 7% increase in fuel consumption. Glass et al. found that the reduction of NO by changing spark timing and exhaust gas recirculation appeared to be indpendent of each other. Thus the vehicle NO control system can use a combination of exhaust gas recycle and spark timing modification to allow NO control with minimal losses in fuel economy.

One of the objections to exhaust gas recycle in the past is that is gives the cars poor driveability. The system described by Glass et al., however, seems to have overcome most of these problems. Only slight traces of surge and stumble were reported for their system. The recycle was shut off during periods of idle, closed throttle deceleration, and periods of low power. At maximum power conditions the recycle can be left in to prevent high NO or cut off to preserve maximum power.

Several benefits related to exhaust gas recirculation have been noted. These include improved vaporization of the fuel (which results in a better distribution of the fuel/air mixture to the cylinders) and reduced ring wear. Kopa et al. (1962) found that ring wear was reduced by 90% at a steady state operation and by about 50% over a driving cycle. No explanation for this effect was given; it was noted, however, that the reduction of ring wear was proportional to the relative peak combustion temperature.

The use of water injection can reduce nitrogen oxides by as much as 90%; the water flow rates required to do this are about the same as the fuel flow rate (Nicholls et al., 1969). Because of the water tank and auxiliary equipment required for this process it appears to be less feasible than exhaust gas recycle. Further, the effects of water on engine deposits and lubrication are harmful to normal engine operation.

Exhaust gas recycle appears to be the control technique for reduction of NO in the engine that will be used in the immediate future (Newhall, 1967, Benson, 1969). The major problems remaining with the practical applications of this technique include the effects of exhaust gas recirculation on carburetor deposits, effects of ambient temperatures on the reduction of NO, and the influence of the recirculation process on ignition and flame propagation.

Another system for reducing the formation of NO in the engine has been described by Newhall and El Messiri (1970). This system uses a divided combustion chamber. Air is throttled into the engine filling both combustion areas. The two combustion chambers are separated by a dividing orifice. Fuel is injected into the primary combustion chamber at an appropriate time in the cycle and ignited by a spark. During the ensuing combustion process the high pressures force the combustion gases through the orifice into the secondary chamber which is the main engine cylinder, bounded below by the piston. Since both combustion volumes contain the air while all the fuel is injected and ignited in the primary combustion chamber the initial combustion process takes place under relatively rich conditions. The flow through the orifice causes a reduction in temperature which quenches the NO formation reactions. The overall equivalence is fuel lean. Consequently after the expansion into the secondary combustion chamber the remainder of the combustion process (i.e. the oxidation of CO to CO_2) takes place at overall lean conditions which favor low CO emissions.

Newhall and El Messiri point out that the primary combustion chamber can be run either rich or lean. In the rich region, NO concentrations generally reach equilibrium amounts, but these are very low. In the lean region the NO kinetics are very slow and the equilibrium concentrations are not achieved before the gases are quenched. This leaves a low overall NO concentration.

This dual combustion chamber configuration is able to simultaneously produce low levels of all pollutants. At one condition of full throttle, steady state operation, the emissions levels were 100 ppm of NO, 3000 ppm of CO and 40 ppm equivalent hexane (by flame ionization detector).

The engine is able to simultaneously reduce these three pollutants for the following reasons. The NO formation is kinetically

limited as described above. The CO is reduced because of the lean overall equivalence ratio. The reason for the low hydrocarbon emissions is not clear, but it is conjectured that it is due to a combination of effects. The main hydrocarbon formation occurs in the quench areas of the primary combustion chamber. The gases that pass from that chamber to the secondary combustion chamber do not come into contact with the walls immediately, thus hydrocarbons passing into the secondary chamber can undergo further oxidation there. Finally, the primary chamber is not directly exposed to the exhaust valve; consequently, only a small amount of the hydrocarbons formed and remaining in the primary chamber are eventually exhausted.

The power output of the dual combustion chamber engine is somewhat reduced over engines of comparable displacement and the octane requirement of this engine is very low. Consequently higher compression ratios could be used. Fuel economy is "consistent with that of conventional spark ignition engines."

The data reported were for steady state operation on a single cylinder engine. The application of this combustion chamber design to the reduction of emissions will depend on the development of multicylinder engines which can reproduce these low emissions over an entire driving cycle.

2.4.5 Emissions Control By Catalysis

The use of catalysts for control of vehicle emissions has been studied for several years. A symposium on heterogeneous catalysis for air pollution control was held in 1968 (Banerjee, 1968), covering all aspects of catalytic control. This includes odor removal from stationary sources and Diesel exhaust as well as pollutant removal from conventional engine exhausts. The latter consists of two basic problems: 1) oxidation of CO and hydrocarbons and 2) removal of NO. The removal of NO by catalytic decomposition has been shown to be too slow to be practicable on known catalysts (Shelef et al., 1969). It is possible, however, to react the NO with other components of exhaust gases such as CO, H_2, and hydrocarbons, forming CO_2, N_2, and water. When doing this it is important to maintain effective control over the initial composition entering the catalyst bed since many of the reducing species will preferentially react with the O_2 present rather than the NO (Baker and Doerr, 1964).

Catalytic hydrocarbon oxidation is a technically important process. Many articles have been written on the subject (e.g. Margolis, 1963). Similarly the CO oxidation is a well studied subject and has been reviewed by Gravelle (1969). Studies of catalytic oxidation for air pollution control were begun in the late 1950s. Cannon et al. (1957) used a single cylinder engine to test various catalysts. Sourirajan and Accomazzo (1961) used a copper oxide-

alumina catalyst to study oxidation of 1-hexane and actual auto exhaust samples. They were able to obtain 100% removal of hydrocarbons from auto exhaust with a catalyst temperature of 400°C. Anderson et al. (1961) studied 30 catalysts for methane oxidation. (They chose methane since this is the hardest hydrocarbon to oxidize catalytically.) Their catalysts included noble metals (Palladium and Platinum) as well as several metal oxides on various supports (e.g. Co_3O_4, Cr_2O_3, Mn_2O_3, CuO, V_2O_5, etc.). They found that the activity of the metals or metal oxides (per gram of active metal) decreased in the following sequence: Pt, Pd, Cr, Mn, Cu, Ce, Co, Fe, Ni, Ag.

Many of these catalysts have the oxidation reaction inhibited by water and carbon dioxide. In most cases this is due to an adsorption of these substances on active sites which would otherwise be available for the catalytic oxidation. Thus the CO_2 and H_2O do not act as a permanent catalyst poison, and, indeed, in some catalysts at higher temperatures, where the adsorption is not important, these substances do not lead to any significant inhibition. For low temperature (< 300°C) catalysts, the inhibiting effect on both hydrocarbons (Klimisch, 1968), and carbon monoxide (Cohen and Nobe, 1966, Thomas, et al., 1969) is noted. This inhibiting effect implies a temperature increase of 30 to 100°C to achieve the same degree of oxidation at given initial reactant concentrations and flow rates.

An early description of a catalytic converter system (Schaldenbrand and Struck, 1964) indicated that none of the catalysts tested would meet the minimum requirements (i.e. California Cycle test with 275 hydrocarbons and 1.5% mole CO) over extended mileage. Recent studies have indicated that catalytic converters that can operate for long lives are possible (Weaver, 1969, Schwochert, 1969). Unfortunately many of these catalysts require noble metals which may not be practical because of cost and availability. The catalyst used by Weaver had 100 - 150 ppm of Palladium and required 2800 gm of catalyst to fill the converter. This implies 0.28 to 0.42 gm of Palladium for a single converter. Weaver also studied the effects of using leaded fuels on catalyst life. He found that the ability of the catalyst to remove hydrocarbons was severely affected by the presence of lead, but the CO oxidation ability was not affected by the lead. The most serious problem found was a catalyst loss due to attrition. A Mobil Research report (1970) describes some results on several unidentified catalysts indicating that there is little difference in catalyst deterioration between lead free and "low lead" (0.5 gm Pb/gal) gasolines. These results are preliminary, however, as the tests have only been run for 18,000 miles.

The possibility of catalytic NO removal by reacting with reducing agents present in the exhaust gases has been reported by

Sourirajan and Blumenthal (1961), Baker and Doerr (1964), and Ayen and Ng (1966). Most of the catalysts used in these studies were copper compounds (oxides and chromites) supported on alumina with various promoters. No precious metals were used. Baker and Doerr tested a $CuO/Co_2O_3/Al_2O_3$ catalyst with exhaust gas from an engine run on leaded fuel for 350 hours. After this test period the catalyst was still able to reduce an initial concentration of 1500 ppm NO by 90%. They found that reducing conditions were required, i.e. the CO would preferentially react with the O_2 present rather than the NO.

If it is necessary to react the NO with some reducing agents in a reducing atmosphere the engine must be run rich so that there is little excess oxygen in the exhaust gases. This would imply a two stage catalytic converter in which the NO is removed in the first stage and air is added between stages so that the oxidation of the CO and hydrocarbons can take place in the second stage. It would be useful to develop a catalyst that would allow simultaneous removal of all pollutants. It would also be useful to develop a catalyst which could remove NO (by reaction with a reducing agent) in the presence of oxygen. Such a catalyst would not impose any restrictions on the engine operating conditions, which, in turn, restrict the choice of other control techniques.

Recently, workers at Ford have studied precious metal catalysts for the removal of NO (Jones, et. al., 1970). They have attempted to find catalysts which could promote the reaction between NO and reducing agents even in the presence of oxygen. They found that under certain carburetion conditions, close to the stoichiometric air-fuel ration, NO could be removed even in the presence of oxygen. If it were possible to maintain such conditions over the complete range of engine operations then a single catalyst might be successful in removing all pollutants from exhaust gases. At lower temperatures ($< 400°F$) the NO is removed by reaction with the H_2 present. The NO/H_2 reaction is selective over the O_2/H_2 reaction over the Platinum and Palladium catalysts. At higher temperatures ($> 600°F$) the removal of NO is believed due to simultaneous reactions in which the CO reacts with O_2, NO, and in the "water-gas" reaction, $CO + H_2O = CO_2 + H_2$. The hydrogen generated in the last reaction can then react with the NO. The NO/H_2 reaction can be poisoned by sulfur in the exhaust gases.

Shelef et al. (1968) have shown that the selectivity of catalysts between the CO/NO and CO/O_2 reaction is dependent on the oxidation state of the catalyst. They studied a series of catalysts consisting of transition metal oxides or platinum supported on 95% alumina-5% silica. They found that the CO/NO reaction was faster than the CO/O_2 reaction on supported chromia catalysts when the two reactions were run independently. When a mixture of $CO/NO/O_2$ was used, however, the CO/O_2 reaction was selected. The authors attribute this result to the following mechanism:

(a) reduction of the catalyst surface by the reducing agent

(b) desorption of the oxidized product

(c) reoxidation of the catalyst surface

When the NO is used as the oxidant, step (c) is the rate limiting step; when O_2 is the oxidant, step (c) is fast but step (a) is the rate limiting step. Thus when both O_2 and NO are present the reoxidation of the catalyst surface by NO does not occur to a significant extent since the O_2 present carries out this step much more rapidly. Consequently the NO is not reacted.

Otto et al. (1969) have studied the reaction between NO and ammonia over a supported platinum catalyst between 200 and 250°C. They found that this reaction is selective even in the presence of oxygen. They give several references to patents that have issued using the reaction of NO and NH_3 for the removal of NO from industrial effluents and automotive exhausts.

It appears that the use of catalysts offers interesting potential for very low levels of all emissions. Before this promise is realized, however, it will be necessary to assure that the catalytic systems can withstand the rigors of automotive application for several thousand miles.

2.4.6 Developments in Low Emissions Systems

A report by the Technical Advisory Committee of the California Air Resources Board (1969) described several engines and vehicles that have demonstrated low emissions levels. The emissions from these vehicles are summarized in Table II.

Table II. Low Emissions Systems (Gm./Mi.)

	Sun Oil	Reactor	Catalyst	Synchro	Ethyl	Du Pont	Proposed 1975 Calif. Standards
Hydrocarbons	0.7	1.5	1.7	0.25	< 0.7	0.2	0.5
Carbon monoxide	12.0	< 20.0	12.0	7.0	< 10.4	12.0	12.0
Nitrogen oxides	0.6	< 1.3	1.0	0.6	< 2.5	1.2	1.0

The Sun Oil car uses a homogeneous exhaust reactor with air injection for reduction of hydrocarbons and CO. The engine is run very rich and engine timing is modified to obtain low NO levels. Fuel consumption is increased by 11% because of the rich engine operation.

The Chrysler-Esso data are generally considered to be obtained with dynamometer tests rather than on actual vehicles. The "reactor" system used a homogeneous exhaust reactor to reduce hydrocarbon and CO emissions and exhaust gas recycle to lower the NO. No details on the catalytic system were given. The "synchro" system used the reactor concept of Glass et al. (1970) described in the section on homogeneous exhaust reactors. This was coupled with exhaust gas recycle for reduction of nitric oxide. The fuel consumption was found to increase as the emissions levels were decreased. Fuel consumption for the best control system was 21% greater than that for normal vehicle operation.

The Ethyl car was run with high velocity carburetor, optimized spark timing, and a homogeneous exhaust reactor. The overall mixture fed to the engine was fuel lean; consequently, it was not necessary to use air injection into the exhaust reactor. Driveability and fuel economy were reported to be unchanged from those of a conventional vehicle. Although the hydrocarbon and CO reductions are sufficient to meet the 1975 California requirements, much improvement is required for NO.

The results from Du Pont were for a vehicle fitted with a homogeneous exhaust reactor for hydrocarbons and CO and exhaust gas recycle to lower the nitric oxide. Although this car achieves excellent hydrocarbon levels its NO levels cannot meet 1975 California standards.

It can be seen from the above summary that the general approach for the overall systems is the use of a homogeneous exhaust reactor for reduction of hydrocarbons and CO, coupled with exhaust gas recycle for NO reduction. Engine operation is usually rich to obtain an initially low level of NO and provide "fuel" for the exhaust reactor. Although some work on catalysts has been reported and one catalytic engine system has been reported by the Chrysler-Esso program, it appears that catalytic systems have not yet been brought to the same stage of development as the combined exhaust reactor/exhaust gas recycle systems.

2.5 DIESEL EMISSIONS

2.5.1 Diesel Combustion

Exhaust emissions from diesel engines are primarily a local nuisance due to odor and smoke. Their contribution to the overall pollution picture is relatively small due to their low usage. (Diesel fuel accounts for about 5% of the fuel sales in most metropolitan areas.) Hurn (1969) has reviewed the role of the diesel in air pollution.

In the diesel, a constant amount of air flows into the cylinder for each charge. The air is compressed using relatively high compression ratios (ca. 20:1) and the fuel is injected near the end of the compression stroke. The power output of the engine is controlled by regulating the amount of fuel. The ensuing combustion process is one of the heterogenous droplet combustion. Two basic types of combustion chambers, "direct injection" and "precombustion" are used. In the former system the fuel is directly injected into the main combustion volume. In the precombustion system the fuel is fed into a relatively small precombustion chamber. Here the fuel ignites and burns under rich mixture conditions since all the fuels is injected into precombustion chamber which contains only a small fraction of the total air.

Because the airflow is constant while the fuel flow varies the equivalence ratio in the diesel can vary widely. Typically the engine will operate between equivalence ratios of 0.15 (at idle) to 0.8 (at full load). Because of the large amounts of excess air possible under low load operations it is important to normalize measured concentrations of exhaust emissions to obtain an accurate measure of the true emissions mass production rate.

The high temperatures produced by the higher compression ratios combined with the large amount of oxygen can lead to a production of large amounts of nitrogen oxides. On the other hand the lean mixtures form relatively small amounts of CO and hydrocarbons. No complete analyses of the hydrocarbon reactivity from diesel exhaust have been made.

2.5.2 Hydrocarbons, CO, and Nitrogen Oxides

Hurn (1969) reports various "normalized" concentrations of ppmC. These are concentrations of C atoms in hydrocarbons as measured by a flame ionization detector. To obtain concentrations in terms of the usual ppm n-hexane as measured by the NDIR these concentrations should be divided by two factors, a factor of 6 for the carbon atoms and a factor of from 1 1/2 to 2 for the use of the FID which gives a higher reading. Typical concentrations for 4-cycle diesels are 300-3000 ppmC (FID). The lower concentrations are for full load, the higher concentrations are for idle. One cannot readily compare these steady-state results to the usual automotive

standard of 180 ppm equivalent hexane (NDIR) over a specified driving cycle. In any event, the 300 ppmC (FID) is something like 300/(6)(1.8) = 30 ppm equivalent hexane by NDIR. Thus the typical hydrocarbon concentrations are indeed low.

Similarly CO concentrations are reported to be between 0.04 and 0.78 mole percent. These are also very low, although they are close to or above the proposed 1975 California standard (12 grams per mile CO is equivalent to an exhaust concentration of 0.5 mole percent for a 4000 pound car with an automatic transmission).

Normalized values of aldehyde concentrations vary between 4 and 437 ppm. The latter is exceptionally high and considering all modes of engine operation more typical values would lie between 50 and 75 ppm. Normalized concentrations of oxides of nitrogen in the exhaust are between 1500 and 5000 ppm. In the diesel engine a significant portion of the nitrogen oxides emissions may be in the form of NO_2 due to low temperature oxidation of the NO. The oxidation of NO to NO_2 typically takes place in the exhaust system. Reckner et al. (1965) found that the NO_2/NO_x ratio varied from 10/21 at no load to 26/1066 at full load. Harkins and Goodwine (1964) found similar results. Both groups of experimenters commented on the importance of the timing of the analysis for the nitrogen oxides as the NO is continuously undergoing oxidation to NO_2 in the sampling and chemical analysis system. This is due to the high concentrations of NO present. This is different from the results that would be obtained if the exhaust were emitted directly into the atmosphere where rapid dilution takes place. Thus the NO_2 concentrations measured are probably higher than the NO_2 produced during normal vehicle operation.

Perez and Landen (1968) have studied the emissions from a precombustion diesel. They found that the emissions of all species were generally lower. They normalized their emissions measurements on the basis of fuel consumption and found that the hydrocarbon emissions per unit fuel burned were about 10% of those from gasoline engines. They also found that the odor was only about 10-20% of that from direct injection engines.

2.5.3 Odor

The odor and smoke problems have received the most attention from investigators of diesel emissions. In an early study of odor components, Reckner et al. (1965) bubbled the exhaust gas through a 5% aqueous sodium bicarbonate solution to collect odorous compounds. (They found that such a process removed most of the odor from the exhaust.) They then extracted compounds from the resulting solution by using various organic solvents, and used a liquid chromatographic column to separate and collect various compounds. The mass spectra of the separated compounds were obtained. A large

number of the mass spectra obtained could not be matched with any known spectra.

Other organizations have investigated the separation and identification of odiferous compounds in diesel exhaust. Arthur D. Little, Inc. (1969) developed an analysis system, again using chromatographic separation and mass spectrometric identification, to characterize the chemical odor species. They found that some of the individual odorous components may be present, after dilution in air, in concentrations of 1 part per trillion. The Illinois Institute of Technology Research Institute (1969) has also developed a chromatography-mass spectrometry system for study of diesel odor. At last report positive identification of the specific compounds was beginning.

Vogh (1969) investigated the concentrations of specific compounds in diesel exhaust. He presented his odor panel with pure compounds at the highest levels that these compounds were found in the exhaust, diluted at 100:1 to account for atmospheric dilution. He found that the "common impression of aldehydes being the major odorants in diesel exhaust is incorrect, at least for most aldehydes known to be present in diesel exhaust." He also found that sulfur oxides and nitrogen oxides made negligible contribution to diesel odor except for a small contribution for NO_2 formed during idle operation. Vogh suggests 5 possible sources for odorous compounds: 1) hydrocarbons either as present in the original fuel or as modified during combustion, 2) organic oxygenates other than carbonyls, 3) high molecular weight carbonyls that would be trapped out in the water scrubbing system used in Vogh's experimental sampling system, 4) reactive compounds that could be destroyed or altered in the sampling process, and 5) sulfur and nitrogen compounds (other than the oxides).

Southwest Research Institute (1969) has tested the effectiveness of catalytic mufflers and exhaust dilution systems for control of odor. Details of the catalyst were considered proprietary and were not given in the report. It was noted, however, that the muffler material was in the form of a honeycomb rather than pellets. The muffler gave improvement of exhaust odor in all operating conditions, except during idle when one of the two buses tested had higher odor with the catalytic muffler. Tests on a "DEOX" system which used air dilution in the exhaust for odor control had only a partial effect on odor and appeared not to merit further consideration.

2.5.4 · Smoke

Diesel smoke is generally described in three categories: 1) white smoke, 2) blue smoke, and 3) black smoke (Hurn, 1969, Miller, 1967). The white smoke comes from unburned fuel fog which may

contain condensed water vapor. It is due to cold engines immediately after startup and usually disappears in warm engines. Blue smoke is the result of combustion of excessive amounts of lubricating oil and is an indication of a poorly maintained engine. It is easily cleaned up by replacement of rings or valve guides. The black smoke results from incomplete combustion of the fuel and is of primary concern when one considers the subject of diesel smoke.

The mechanism by which black smoke is formed is not clearly defined. The smoke results from injection of a greater amount of fuel than can be properly burned by the air in the cylinder. Reckner et al. (1965) found that smoke intensity measurements could be correlated with particulate emissions measurements during black smoke conditions. A large fraction (ca. 90%) of the particulates emitted under part load conditions were benzene soluble indicating that they were formed from unburned or partially burned fuel. Polycyclic aromatic hydrocarbons which were considered to be of special interest were measured. They were found to compose less than 0.1% of the total particulate emissions.

The Southwest Research Institute report mentioned above also studied the problem of diesel smoke. They found that derating the engine made significant improvements on smoke emissions from engines with initially high smoke levels. Engines which produced little smoke at rated power showed no significant improvement by derating. They also conducted a six-month, five-truck test of a commercial barium additive for smoke suppression. The additive reduced smoke to 1/2 - 1/4 of the smoke level with untreated No. 2 diesel fuel. The final report, however, warns against extrapolating the results of this fleet test to other engines.

The smoke suppressant additive has been described by the Lubrizol Corp. (Miller, 1967). On tests of 26 different makes of engines they found that the barium additive reduced black smoke on all engines. Miller postulates the smoke suppression mechanism as being due to an inhibiting effect that the barium has on the decomposition and dehydrogenation of the fuel in rich regions of the combustion chamber. The barium thus inhibits the formation of the smoke particles as opposed to catalyzing the oxidation of these particles after their formation. The latter mechanism is rejected by Miller on the basis of experiments in which other metals, which are known to catalyze the oxidation of carbon particles, were used as fuel additives. These metals actually increased the smoke formation. Miller further concludes that the additive offers "extra benefits in engine cleanliness and wear reduction," and that "no appreciable changes in exhaust gas analysis have been observed." General Motors Detroit Diesel Division, however, reports that they cannot recommend use of the additive in their engines because of excessive ash deposits attributed to the use of the additive (Brandes, 1970). Several people

have been concerned about the toxic effects of barium in the exhaust of diesels using this metal as a smoke suppressant (Southwest Research Institute, 1968), but Golothan (1967) has estimated that the average person would receive 0.0005 mg of soluble barium per kilogram of body weight per day under the "worst possible conditions." He says that this amount "is not considered to be of significance."

Despite all the apparent difficulties in the production of smoke by diesel engines and the use of additives to suppress smoke, tests made by the New Jersey inspection program (Elston et al. 1969) showed that "engines in proper mechanical condition and operating in the proper fuel-to-air ratio range do not inherently produce excessive exhaust smoke." It appeared that throughout this New Jersey test program that there was a predominant tendency for truck operators to increase the output of their engines by operating at higher fuel/air ratios than those specified by the engine manufacturer. This produced a marked increase in smoke intensity. The "cure" to diesel smoke, then, appears to lie largely in the proper operation of existing engines.

2.6 GAS TURBINES

2.6.1 General Features

There are features that are characteristic of gas turbine engines that warrant consideration of this engine as a replacement for the conventional piston engine as prime mover of ground vehicles. Continuous combustion of overall air rich fuel mixtures promotes more complete combustion and, hence, lower emissions levels. Gas turbine engines are generally lighter in weight than piston engines of comparable horsepower, especially at higher horsepowers. Gas turbines are mechanically simpler than piston engines and operate with little vibration. Gas turbines can also operate using a wide variety of fuels. Typical emissions levels reported for three gas turbine vehicles (Technical Advisory Committee, 1969), for hydrocarbons, CO, and NO, respectively, 0.5, 3.0, and 5.2 for vehicle "A," 1.2, 7.0, and 1.3 for vehicle "B," and 0.7, --- and 0.8 for vehicle "C."

An unfavorable aspect is the present high unit cost of gas turbine engines due primarily to the expensive high temperature metals required. In light of the ever increasing production and maintenance costs of the conventional piston engine and the probability of reduced cost of gas turbine engines resulting from large scale mass scale production, cost may not be such a disadvantage in the future.

The primary application of gas turbine engines at present is in the field of aircraft propulsion. Gas turbines are also increasingly being used by public utilities to operate generators for providing peak power requirements. Initial vehicular applications of gas turbines will be in trucks, buses, and other large vehicles, where the turbine can compete economically. For example, the General Motors gas turbine (GT-309) is scheduled for initial production on heavy-duty vehicles in mid-1971. Rated at 280 horsepower, the GT-309 weighs half as much as a diesel piston engine of equal power (General Motors Research Laboratories, 1969).

The gas turbine exhaust emissions that are of prime concern as air pollutants are oxides of nitrogen, and particulates (smoke). Other pollutants that are emitted in relatively small amounts are hydrocarbons, CO, oxides of sulfur, adehydes, aerosols, and odor. Comparison of pollutant levels with those emitted from piston engines must be done on a basis which accounts for the high air dilution of turbine exhausts resulting from high excess air used. (This is done to obtain lower turbine inlet temperatures.) Comparison can be made on a mass basis (mass of pollutant/mass of fuel or mass of pollutant/mile traveled) or some other suitable emission index.

2.6.2 Oxides of Nitrogen

The formation of oxides of nitrogen is a major pollutant problem of gas turbine engines. Both nitrogen oxide (NO) and nitrogen dioxide (NO_2) are emitted but NO is the dominant species measured in turbine exhausts. NO emissions from some gas turbine engines, based on fuel consumption, approach those from conventional spark ignition piston engines.

Smith et al., (1968) measured NO concentrations in the exhaust of gas turbine engines and from a laboratory combustor. From observed variations in NO levels he concluded the possibility of engine design influence on NO formation. Cornelius et al., (1967) showed the dependence of NO exhaust concentrations on several burner design and operating parameters. NO concentrations increased with increasing fuel-air ratio and with turbine inlet temperature. NO emission was also affected by fuel nozzle spray configuration and atomizing air pressure.

Sawyer and Starkman (1968) observed that probable future improvements to gas turbine engines will favor increased formation of nitrogen oxides. These improvements are: higher combustor inlet air temperatures (arising from improved regeneration, higher compression ratios, or greater aircraft speeds), higher combustor pressures and temperatures and higher turbine inlet temperatures.

Sawyer et al., (1969) state that the maximum local temperature within the combustor controls the NO emission level but that

factors controlling that temperature are not completely understood. A fuel-rich primary combustion zone would not itself necessarily limit NO formation (by reducing the primary combustion zone temperature). As air is added the mixture would eventually attain stociometric proportions and the associated high temperatures. Rather, it was suggested that a lean combustion zone would be an answer to lower NO emissions.

Perhaps optimization of low NO emission combustors will depend on the development of adequate analytical combustor models by which mixture patterns and compositions within a combustor could be predicted. Hammond and Mellor (1970) are currently engaged in the development of such a model. No effective means for control of NO emissions has been found.

2.6.3 Smoke

Smoke, the other major pollutant from gas turbines, is mainly a problem in aircraft engines. It is the result of small particles of almost pure carbon present in the engine exhaust. The structure and composition of these particles is well known. Measurements of particulate sizes in the exhaust of gas turbines have been obtained by DeCorso et al., (1970), Durrant (1968), Faitani (1968) and Lieberman (1968). The composition of smoke particles has been established by some of these investigators and earlier by Shalla and Hibbard (1957) and Thomas (1962). Reported particle sizes ranged between 0.01 and 1.0 microns. It was generally agreed that smoke particles consist of approximately 96% carbon by weight and the remainder is composed mainly of hydrogen and oxygen. The density of smoke particles in engine exhaust is low but the sizes are such that even in low concentrations their presence is highly visible. Experimental studies attribute the high visibility to the fact that particulate sizes are of the same magnitude as the wavelength of visible light.

Smoke is formed during combustion but the exact process is not fully understood. There is, however, general agreement that carbon is formed where rich fuel-air mixtures exist. In such oxygen deficient regions carbon, instead of oxidizing, agglomerates to form smoke. Heywood et al., (1970) observes that smoke formation studies have basically been of three types: observations of simple laboratory flames, studies of combustors and gas turbine engines and chemical kinetics studies. MacFarlane et al., (1964) and Shalla and Hibbard (1957) examined carbon output from laboratory flames and found carbon formation to increase with increasing pressures and overall equivalence ratio. These results are consistent with chemical kinetic predictions. Studies of carbon formation in combustors and measurements from gas turbine exhausts confirmed these results. Faitani (1968), Toone (1968) and Butze (1952) showed that carbon content in combustors exhausts increased

with increasing operating pressure. Tests of full scale gas turbine engines conducted by Faitani (1968) and Durrant (1968) have shown the same relationship between compressor pressure ratio and carbon levels in engine exhaust. Equivalence ratio in the primary combustion zone has been shown to effect carbon formation in studies by Faitani (1968) and Gleason and Faitani (1967). Increased equivalence ratio resulted in higher carbon levels. Tests of gas turbine engines have confirmed this trend. Faitani (1968) reported a reduction in carbon with an increase in temperature at combustor exit. Higher temperatures cause more of the carbon to oxidize.

The elimination of smoke is desired mainly because of its adverse visual character and also because of its contribution to particulate fallout. Awareness of these two aspects of carbon in turbine exhaust is acute at airports where both have been the cause of complaints and criticisms directed at the aircraft industry.

Elimination of smoke has been approached from two directions: use of smoke suppressing fuel additives and fuel combustor design modifications. Recent studies at Pratt and Whitney Aircraft have shown that the use of fuel additives can effectively reduce smoke. However, these additives also create side effects which would prohibit widespread usage. Additives lower engine performance by creating engine deposits or by causing corrosion of engine parts, or they create exhaust constituents even less desirable than smoke.

The other approach to smoke reduction is by combustor design. Faitani (1968) found that a promising technique for smoke reduction was to reduce fuel-rich areas in the primary combustion zone by premixing some of the fuels with air prior to injection into the combustion chamber. Bahr et al. (1969) reports that projects conducted at General Electric have emphasized the importance of rapid mixing of fuel and air and of reducing the fuel-air ratios within the primary combustion zone. General Electric tested engines incorporating these smoke reducing design criteria and found these engines to exhibit non-visible smoke emissions. No sacrifice of engine performance characteristics was necessary. Reductions in smoke levels have been reported by Pratt and Whitney Aircraft for recently manufactured engines.

Visible smoke appears to be no longer a serious problem. Reported successes in reducing smoke from operational turbine engines attest to this.

2.6.4 Hydrocarbons and Carbon Monoxide

Inherent from the combustion conditions of gas turbine engines are low exhaust levels of unburned hydrocarbons (HC) and carbon

monoxide (CO). Air-fuel ratios as much as ten times greater than the stoichiometric ratio and constant high temperatures ensure near complete combustion. Also, the absence of severe wall quenching zones in combustion regions is favorable to the reduction of hydrocarbons.

Durrant (1968) showed variations in temperatures within a combustor from the center to the outer wall at idle condition. Low temperatures at the wall due to ingestion of air to cool the wall resulted in 20% unburned fuel at the wall. HC in the exhaust were negligible at top speed conditions. Durrant suggested a practical solution would be the annular combustion chamber which would require less cooling air because of reduced wall area.

Sawyer et al., (1969) plotted the axial distribution of HC and CO concentrations measured from a laboratory combustor. It was concluded that hydrocarbons would under most conditions be reduced to low concentrations in the combustor and that wall quenching was instrumental in preventing further oxidation of CO. Cornelius et al., (1967) cited an efficient air atomizing fuel nozzle as being the predominant factor in reducing HC emission at low speed and power conditions for a vehicular regenerative gas turbine. These low speed "off-design" operating conditions are the major problem in CO and hydrocarbon emissions.

2.6.5 Sulfur Oxides, Aldehydes, and Odor

These emissions are relatively minor from gas turbine engines. Cornelius et al. (1967) measured exhaust formaldehyde concentrations from the General Motors GT-309 gas turbine. They were able to reduce formaldehyde below two parts per million by using a centralized spray nozzle for the fuel and running the turbine inlet temperature above 1200°F. They reported no odor in the direct exhaust gas from the turbine. (This is in contrast to the usual odor studies where the exhaust gas is diluted before odor is measured.)

Although odor is not generally a problem with gas turbines for ground applications, aircraft gas turbines give off a kerosine-like odor which permeates most airports. In a comprehensive study of aircraft emissions by the Northern Research and Engineering Company (1968) no information on the nature of aircraft exhaust odor was found.

Sulfur oxide emissions are a minor problem. The cure for sulfur oxide emissions from gas turbine engines is the same cure required for all engines: removal of sulfur from the fuel.

2.6.6 Summary

The gas turbine engine is the most likely engine to be used as a substitute for the current spark-ignition piston engine. Its

emissions of all pollutants are generally low; the only compound that appears to present a problem is nitric oxide. The immediate applications of gas turbines to passenger vehicles is limited because the engine cannot be produced at lower costs, but gas turbines will be used soon in heavy duty vehicles. Perhaps experience gained in mass production of these large size engines will lead to use of the gas turbine in passenger cars.

2.7 EXTERNAL COMBUSTION ENGINES

2.7.1 General Features

In an external combustion engine the combustion gases are not the working fluid (i.e. they do not have direct contact with the moving parts of the engine); these gases are used to transfer heat to the actual working fluid. Because of this the combustion process in all external combustion engines are basically the same, and these processes can be studied without considering the actual engine.

The external combustion engines have a continuous combustion process similar to that taking place in the gas turbine combustors. The combustion takes place at atmospheric pressure; there is no compression work to raise the temperature of the gases prior to combustion. Consequently the peak temperatures attained in such combustors can be lower. These temperatues can be increased by preheating the incoming air. These engines can burn a wide range of fuels, and there is no limitation on the overall equivalence ratio that the combustion system uses. Consequently external combustion engine combustors can be operated in an overall very lean region where low emissions of all pollutants are favored. It is necessary to have some local regions in the combustor closer to stoichiometric to produce high temperatures to give adequate heat transfer to the working fluid. This heat transfer lowers the combustion gas temperature. If this can be done rapidly it is possible to reduce NO formation because of the relatively slow NO kinetics. All of these factors, lower temperatures, very lean overall equivalence ratios, and immediate heat loss reducing residence time at high temperatures favor low emission levels. The two basic engine types are usually described by the names of their idealized thermodynamic cycles, the Rankine engine and the Stirling engine.

2.7.2 Rankine Engine

The Rankine engine is commonly called the steam engine because the principle working fluid for applications of this cycle is water. Steam cars, of course, were in wide use in the early 1900's, but they were unable to compete with internal combustion engines because of the steam engine's size, cost, and complexity. Recent

proponents of steam cars claim that applications of modern technology to steam cars could make them competitive, especially when very low emissions are desired.

Emissions data on steam cars are somewhat anomalous. In one government publication (Hearings, Magnuson-Muskie, 1968) emissions measurements on a Williams Brothers steam car were interpreted by the Williams Brothers to give hydrocarbon, CO, and NO emissions of 0.2, 1.0, and 0.15 grams/mile, while interpretation of the same data by General Motors gave emissions of 0.7, 4.0, and 0.4 grams/mile for hydrocarbons, CO, and NO. General Motors has reported the construction and emissions testing of a steam car (Vickers et al., 1970). They estimate that the mass emissions rate would be 0.5, 8.0, and 2.0 grams/mile for hydrocarbons, CO, and NO. Starkman et al. (1970), have estimated that the mass emissions from this car would be 0.13, 2.4, and 1.0 grams/mile for hydrocarbons, CO and NO. In any event it is readily seen that the steam car is an inherently low emissions vehicle. These emissions can probably be reduced further by burner redesign.

Bjerklie and Sternlicht (1969) have published an optimistic comparison of Rankine and Otto cycle propulsion systems. They conclude that water is the best working fluid currently available, but they set up specifications for the "ideal" working fluid. This "ideal" fluid would be an organic liquid which would provide lubrication of the engine. (One of the difficulties with steam engines is the problem of lubricating the moving parts; typically one uses low RPM to reduce wear and a separation system to remove lubricating oil from the condensed steam.) One other property of the "ideal" fluid is a low freezing point to allow its use in cold climates. Another objection to the steam engine is its long warmup time. Bjerklie and Sternlicht have calculated that warmup times of less than 10 seconds are possible. The General Motors SE-101 steam car requires "about one minute" to become operative (Vickers et al., 1970).

The General Motors SE-101 was designed to give performance and accessory packages similar to current automobiles. Accessories included power steering, power brakes, and air conditioning. Since steam engines have high torque at low RPM it is not necessary to have a transmission to power the vehicle and the engine can be shut off during stops in traffic. To do this, however, requires some auxiliary power system for accessories. These include items such as the air blower and pumps for fuel and water which are a necessary part of the engine system. In the SE-101 car a single engine operating continuously was used; a transmission allowed the engine to provide accessory power at idle. This choice was shown to give other benefits to vehicle operation and control. The power plant was installed in a 1969 Pontiac Grand Prix. In order to accommodate the steam power

system it was necessary to increase the length of the engine compartment by 8 inches. The final engine package weighed about 2 1/2 times the weight of a comparative spark-ignition engine. The condenser which was provided was sufficient to condense most of the water, but water was lost during heavy load operation. The condenser was designed so that water replacement would not be required more often than refueling.

The General Motors car is obviously a large, semi-luxury car. It demonstrates that Rankine cycle engines can be effectively used in such vehicles. Of course, the size of the power plant is excessive and the cost would probably be more than for the conventional engine. In addition the fuel economy is less with the steam engine. The Rankine cycle systems will probably find initial public use on larger systems such as buses and/or trucks in which they will be competing with gas turbine engines. More development is needed before the Rankine power plant can successfully compete as the optimum engine for private cars.

2.7.3 Stirling Engines

The other external combustion system given substantial attention is the Stirling engine. This engine uses a gas as the working fluid (usually hydrogen, helium, or air). Although the Stirling engine concept was developed in 1816 and the engine was in use during the first half of the 19th century, it was replaced by the steam engine because the latter could produce more power. Interest in the Stirling engine was revived in 1938 when the N. V. Phillips Company in Holland was looking for a convenient power source for remote electrical equipment. General Motors began work with this engine in 1958 and has tested it in several applications. Although the initial applications were in stationary power sources the Stirling engine is being considered for vehicular applications because of its low emissions.

The historical development, operating principles, and potential applications of Stirling engines have been reviewed by Martini et al. (1969). The Stirling engine is more efficient than the conventional spark-ignition engine, but it has a larger size for a given power output. For outputs of several hundred horsepower, however, the Stirling engine will be comparable in size and weight to a diesel engine (Heffner, 1965). Another important feature of the Stirling engine is that it is inherently noiseless. It is also relatively free from vibration because of the drive system used. One of the main difficulties with application of the Stirling engine is its poor response to changes in load. For this reason the initial applications of this engine, both by Phillips and General Motors, were to stationary power sources with relatively constant loads.

Lienesch and Wade (1968) studied the smoke, odor, noise, and exhaust emissions from a Stirling engine. The engine was run at equivalence ratios of from 0.67 to 0.75, thus the concentrations reported will appear somewhat favorable because of the excess air. At 0.67 equivalence ratio the reported emissions were 2.0 ppm equivalent hexand (NDIR) for hydrocarbons, 200 ppm of CO, and 600 ppm of NO. Converting the emissions data to a grams per mile basis (Technical Advisory Committee, 1969) gave figures of 0.06, 0.3, and 1.0 grams/mile for hydrocarbons, CO and NO, respectively. Thus the Stirling engine can meet the proposed 1975 California standards. It would be necessary to reduce the NO emissions even further to meet the proposed 1980 federal standards. The major problem with application of this engine is cost and ease of control. Control can be made easier by using a hybrid Stirling/electric vehicle (Agarwal et al., 1969), but this system is even more costly.

2.8 ELECTRIC VEHICLES

Replacement of the conventional gasoline piston engine in family car type general-purpose passenger vehicles by an electric power system of comparable cost and performance is not possible at present and it appears that it will not be possible within a decade. Much research, however, has been directed to this end and will continue.

The present state of technology of secondary (rechargeable) batteries is such that successful application of this power system to special-purpose vehicles has been achieved. These vehicles are usually small in size and have low top speeds and limited speed. Many have been built and tested. Some are being marketed. A report from the Japan Automobile Manufacturers Association, Inc. (1968) listed current prototype electric vehicles in Japan. Included were 14 battery electric prototype vehicles, some of which were in individual use. One design was reported being under production and being marketed. Young (1969) gives the extent of battery electric use and development. Young relates that 40,000 electric trucks were currently operating in England. One manufacturer offered 11 models with operating costs reported at half those of comparable gasoline piston engine vehicles. Young also tells of wide use of fork lift trucks and personnel carriers, and also of the probable manufacture of a lead acid battery passenger expected in 1969. One third of all in-plant trucks in this country are battery powered with operation and maintenance costs about 40% less than those of comparable gasoline powered trucks (Young). Young lists 18 operational electric passenger cars produced from 1964 to 1968 in this country of which two were marketed.

In any vehicle propulsion system two important parameters are the energy density and the power density. A high energy density is required to give a vehicle an adequate range. A high power density is required to give the vehicle enough power for acceleration and hill climb. These parameters become especially important in the case of batteries. For a combustion engine energy density is easily achieved through the liquid fuel. The power density is a function of engine design. For batteries, however, the density is a function of the battery materials and the rate at which the energy is used. Thus for batteries the energy density and power density are closely related. Further, the energy density decreases as the power density increases. For any given battery system it is necessary to know the energy/power characteristics to predict the performance of the battery in driving a vehicle. The limited speed and range of current electric vehicles are due to the low energy and power densities of their battery systems.

Because battery powered vehicles developed to date have low speed and range they have not been considered as a complete replacement for current engines. They are, however, a potential specialized substitute of particular usefulness in an urban environment where low speeds and ranges are acceptable and where potential reductions in air pollution by widespread use of such vehicles would warrant consideration. Douglas (1967) concluded that the lead-acid battery, since it is lower in cost by factors of from 2 to 20 than other battery types, is most attractive for electric vehicle application and will continue to be so for the next few years.

In the "Morse report" (U.S. Department of Commerce, 1967), a thorough review of the state of the art in battery and fuel cell development is given. It was concluded that fuel cells provide greater vehicle range than any known battery system and would be very low pollutant sources. Such cells, however, are not at a state of development where they could be used to power private passenger vehicles. Cost of fuel cells are high and for these systems to be practical, costs must be reduced by a factor of from 10 to 100 (Morse report). There is little hope for eventual vehicle application for those fuel cells containing precious metal electrocatalysts. Most fuel cells do contain precious metal electrocatalysts (usually platinum). Unless required concentrations of these metals are drastically reduced, these fuel cells cannot be used on a wide scale due to high costs and short supply. Elimination of precious metals from fuel cell systems is imperative.

Hybrid electric systems would incorporate both batteries and fuel cells. The batteries provide the high power density for acceleration and hill climbing; the fuel cell has the necessary energy density to give the vehicle an acceptable range. Although

this combination sounds attractive the cost would probably be too high for widespread use in private passenger vehicles.

One conclusion of the Morse report was that adequate electronic control of an electric powered vehicular system is possible with current technology. Satisfactory electric motors are also available. This has been demonstrated by the operation of electric vehicles such as the General Motors Electrovair II (Rishavy et al., 1967).

Arthur D. Little, Inc. (1968) has prepared a comprehensive report of the prospects of electric powered vehicles and of the research requirements for successful operation of such vehicles. The final report recommends further work in batteries having alkali-metal electrodes and molten-salt or ceramic electrolytes. These batteries were considered to be the only ones having sufficient energy and power density for successful application in vehicles. The same report also states that the prospects of the fuel cell for vehicular application are unfavorable because of its extra complexity, cost, and low power density.

Finally, it should be noted that the electric car is not a panacea for pollution control. It will reduce the vehicular pollution only at an increase in pollution from power plants. Good control of power plant emissions (both chemical pollution and radiation pollution) is a prerequisite for widespread use of electric cars.

2.9 HYBRID SYSTEMS

Hybrid propulsion systems involve the use of two different types of engines to power a single vehicle. The idea of such a system is to match the two components so that the advantages of one part fill in the disadvantages of the other. Many different systems have been proposed. These can be grouped into three basic types: heat engine/heat engine, heat engine/electric, and electric/electric.

The electric/electric hybrid typically involves a battery and a fuel cell as the two components. As mentioned in the previous section, this combination uses the fuel cell to provide energy storage capability and the battery to obtain peak power.

The heat engine/heat engine systems are designed to obtain the maximum mechanical energy from the combustion gases. As an example, Bjerklie (1970) has proposed a hybrid system whose basic component is a conventional spark ignition engine with a homogeneous exhaust reactor. Instead of using the exhaust reactor as

a simple control device, Bjerklie proposes using it as the combustor for a Rankine cycle engine which could be used to provide accessory power. Such a system, with exhaust gas recycle for control of nitrogen oxides, would afford control of all emissions with little reduction in fuel economy. The initial cost of such a system would be higher, however.

The majority of attention given to hybrid vehicles has been to the heat engine/electric combination. In this system the heat engine does not deliver power directly to the wheels; instead, it is used to drive a generator. The generator power can be used to drive the electric motor (or motors) which provide power to the wheels or to charge a battery (or both). The engine is run at a single, constant, steady-state operating condition. During periods of low load the power output from the engine/generator that is not required to drive the vehicle is used to charge the battery. During periods of high load energy to propel the vehicle is obtained from both the engine/generator and the battery. Thus the engine puts out a constant amount of power and the battery acts as a reservoir for the excess or deficit power caused by differences between engine output (constant) and required power (variable).

By running the heat engine at one steady-state operating condition the emissions can be greatly reduced since a large amount of emissions are due to transient operating conditions. Also, since the power output of the engine will be much smaller than the peak power requirement the emissions will be reduced. This reduction will be due to lower mass flow rates of exhaust and lower combustion temperatures leading to reduced NO emissions. Finally, the engine can be optimized to run at its single design operating condition. This is in contrast to normal heat engine vehicles where design compromises must be made to give low emissions over the wide range of engine operating conditions necessary for normal vehicle operation.

A final hybrid system which does not fit into the classification system given above is the heat engine/flywheel combination. Here the inertia of the flywheel is used to store the excess energy put out by the engine at low load. A Battelle Memorial Institute (1968) report describes some such systems for remote power uses in aerospace applications. One of the difficulties associated with such systems is the low energy density available in the flywheel.

The primary difficulty with all hybrid systems is initial cost. It is necessary to provide essentially two power plants for a single vehicle. Consequently hybrid systems will find practical application only if emissions standards are so strict that they cannot be economically met with a single power plant.

2.10 ANALYSIS OF VEHICLE EMISSIONS

2.10.1 Driving Cycles

In addition to the usual problems of sampling and chemical analysis of exhaust gases from combustion processes the measurement of vehicle emissions presents an additional problem: the specification of the driving cycle. This cycle is a set of operating conditions designed to model the typical operating conditions of a vehicle during its use by the average motorist. The initial driving cycle, now called the California cycle, was based on tests of driving habits made in Los Angeles during the mid 1950's. This cycle formed the basis of the federal emission standards established nationwide in 1968.

It is important that the driving cycle specified in the law for emissions standards accurately represents typical vehicle use patterns, otherwise the reduction in emissions measured on the test cycle will not be realized in practice. Bush et al. (1968) developed "commuter cycles" based on driving routes which involved substantial freeway driving. Their cycles had average speeds of 40-45 mph and reached peak speeds of 70 mph. They compared a 1957 Chevrolet and a 1966 Plymouth equipped with the first version of the Chrysler Cleaner Air Package (CAP). They found that "on the freeway the exhaust compositions of the 1957 Chevrolet and the 1966 Plymouth are practically indistinguishable except for the high NO concentrations in the Plymouth exhaust." When the exhaust gases were used in irradiation chamber studies to measure their smog forming potential in terms of oxidant concentration, they found a reduction in O_3 content, but this was attributed to "an increase in NO rather than any decrease in hydrocarbon concentrations." At the same time, they found that the 1966 car met the state standards on the 7-mode cycle.

Various new test cycles have been proposed. The State of California has proposed a driving cycle based on morning commuter traffic in Los Angeles called the LA-4 cycle (Hass et al., 1968). The morning commute traffic was chosen as the basis of the cycle since this traffic represents a large portion of the daily emissions and these emissions enter the atmosphere with a large amount of subsequent time available for photochemical reaction.

The federal government is considering the adoption of a lengthy test cycle which would require nearly 20 minutes to complete and involves speed changes every few seconds. It appears that current studies will lead to a new driving cycle for use in the next few years.

Driving cycles can be described as either "open" or "closed" cycles. In an open cycle samples are taken from the exhaust during portions of the cycle, analyzed for emissions concentrations continuously, and assigned a weighting factor to account for the contribution of that operating mode to the overall emissions. The final emissions figure is just the weighted average over the portions of the cycle which are sampled. In this case, the sampling is easy since it is not necessary to use a proportional sampler and those portions of the cycle which are not being considered can be simply ignored in the final calculation. In a closed cycle the entire exhaust or a sample flow which is proportional to the total exhaust flow is collected and mixed in a bag during the entire cycle. The concentrations of the bag contents then represents the average concentration over the cycle (Mick and Clark, 1969).

The cycles mentioned above are designed for complete tests either for vehicle certification (which is done on prototype vehicles before beginning the actual production, for assembly line tests, and for surveillance tests of vehicles on the road. Several states have proposed inspection programs to inspect the emissions from every vehicle prior to annual registration. For this purpose, it has been necessary to develop so-called inspection cycles which can give a representative measure of the vehicle's emissions in a relatively small time (Pattison et al., 1968). One question that is still unanswered is that of a "diagnostic" cycle that can be used for maintenance. Currently automobile dealers are checking the idle CO concentrations when adjusting carburation. It would be useful to set various operating points to allow automobile repair shops to properly maintain cars for low emissions.

2.10.2 Chemical Instrumentation

The measurement of exhaust emissions has been done primarily by use of the non-dispersive infrared analyzers. These analyzers are used for measurement of CO, total hydrocarbons, and NO. They are also used to measure CO_2 in order to normalize exhaust concentrations to take excess air into account. One obvious disadvantage of this measurement technique is that a separate analyzer is required for each compound that is measured.

The NDIR has proven to be an effective analyzer for CO and CO_2. The use of this analyzer for NO is relatively new and appears to be satisfactory. The analysis for total hydrocarbons only measures the hydrocarbons which have infrared spectra similar to n-hexane, the compound used in the detector. This has been shown (Jackson, 1966) to be a poor measure of olefinic hydrocarbons which are the main contributors to photochemical smog. Because of this it has been proposed that the hydrogen flame ionization detector

(FID) be used to measure total hydrocarbons. This instrument has been shown to give a good count of the hydrocarbon carbon atoms present in the exhaust stream. Further, this instrument is not sensitive to CO, CO_2, or N_2. It is subject to slight interference from O_2, but this is easily overcome. The FID is not sensitive to oxygenated materials. It does not measure carbon atoms existing in C=O bonds; thus it is insensitive to formaldehyde and only gives a partial indication of the other oxygenated material (Teague et al., 1970).

The measurement of oxygenated material in the exhaust is still a subject of investigation (Coordinating Research Council, 1968 and 1969). It seems that some of the proposed control techniques such as the exhaust manifold reactor could lead to the formation of aldehydes through low temperature oxidation. Since these materials are intermediates in the photochemical smog reaction, an accurate measurement of these compounds is important.

The federal government has proposed standards for particulate material in automobile exhaust beginning in 1975. There are currently no known methods for effectively and routinely measuring particulate material in the exhaust. Some work has been done on the measurement of lead (Habibi, 1970), but this is still a research project and not a routine testing procedure.

The measurement of nitrogen oxides from turbine engines has presented difficulties in the past because of the low concentrations present under some conditions. These concentrations which can be as low as 10 ppm are due not only to the large amount of excess air in turbine operation but also to the low production (on an absolute mass basis) of nitrogen oxides. The NDIR has not proven effective in measuring these low concentrations. Static ultraviolet techniques based on the oxidation of NO to NO_2 have been used (Nicksic and Harkins, 1962), but these can be time consuming. Recently a new type of analyzer has been proposed for measurement of low NO concentrations (Fontijn et al., 1969, Stuhl and Niki, 1970). This is based on the continuous reaction of O_3 and NO producing NO_2 where some of the NO_2 will be in an electronically excited state. As this excited NO_2 decays to the ground state it emits continuum radiation which can be measured. The intensity of the radiation can be used as a measure of the NO concentration by suitable calibration.

Although the FID gives a measure of the total exhaust hydrocarbons, exclusive of oxygenated material, it does not distinguish between reactive and non-reactive hydrocarbons. It will be necessary to find a convenient method for measuring exhaust reactivity if this is to be used as a legal emission standard. Currently exhaust reactivity is measured by running a complete chromatographic analysis of the exhaust hydrocarbons (Papa et al., 1968). It is

also possible to make "class" analyses by selective subtraction columns (Klosterman and Sigsby, 1967). Such analyses will give a measure of reactivity (Chipman et al., 1968). Finally, it is possible to use direct irradiation of the exhaust gas. This method gives a direct measurement of reactivity (Dimitriades et al., 1970), but it can be somewhat time consuming.

Most of the instruments discussed so far are for use in research and testing labs. These instruments require some degree of skilled operation and can be expensive. It is necessary to develop instruments that can be used for routine maintenance by relatively unskilled garage mechanics.

Although instrumentation for measurement of vehicle emissions has been in regular use for several years, there are many areas in which improvement is needed. These lie mainly in obtaining a better measure of exhaust hydrocarbons including oxygenates, and in finding a simple method for the measurement of exhaust reactivity.

2.11 FUELS AND ADDITIVES EFFECTS ON EMISSIONS

2.11.1 Fuel Effects

One of the ideas always hoped for by the public is the "clean burning fuel" which will produce no emissions. Although much work has been done investigating the effects of various fuels on emissions there seems to be little difference between various gasoline blends in the production of exhaust emissions. One exception to this statement is the use of natural gas or liquid petroleum (LPG) as engine fuel. These gases have been shown to give sharply reduced emissions, but their use for the general vehicle population is considered impractical since there are not sufficient supplies of these materials available. Also use of these gases is less safe than gasoline, and their use is prohibited in some tunnels. The effects of gasoline composition on exhaust emissions have been studied by various investigators. McReynolds et al. (1968) found that the fuel composition had a significant effect on the exhaust reactivity as measured in an irradiation chamber. Starkman et al. (1970) compared various pure fuels for the production of nitric oxide and carbon monoxide. Specifically they compared a paraffinic fuel, iso-octane (2,2,4-trimethylpentane) with three aromatic fuels, cumene, o-xylene and benzene. No clearcut trends could be found for CO except that benzene tended to produce more CO for rich mixtures than the other fuels. In the case of nitric oxide, however, all the aromatic fuels produced more NO at all equivalence ratios studied, than the iso-octane. A theoretical analysis showed that this was due to a combination of higher peak cycle

temperatures and lower hydrogen to carbon ratios with the aromatic fuels.

Ninomiya and Golovoy (1969) compared iso-octane and a similar olefin, 2,2,4-trimethyl-1-pentene for the production of exhaust hydrocarbons and exhaust reactivity. At lean equivalence ratios they found that the exhaust reactivity was higher for the olefinic fuel, but under rich conditions they found that the reactivity of the exhaust hydrocarbons from the parafinic iso-octane was higher than that from the 2,2,4-trimethyl-1-pentene. Chromatographic analyses showed that this was due to higher concentrations of olefinic exhaust compounds produced by iso-octane. Thus the idea that reduced olefinic content of the fuel leads to reduced olefinic content of the exhaust hydrocarbons is not correct for rich operating conditions.

Jackson (1964) tested gasoline-ethanol fuel mixtures in a single cylinder engine. He compared emissions from a 25 percent weight ethanol in gasoline mixture with those from pure gasoline. He concluded that the fuel mixture showed "no promise" for reducing pollution.

The tests mentioned above have been done primarily on test engines with carefully controlled steady state operating conditions. Dishart and Harris (1968) studied various fuel compositions, varying the concentrations of olefins and aromatics, in a normal, full-range gasoline. They ran tests on a fleet of cars using the driving cycle to measure exhaust emissions. They found small effects of aromatic content on hydrocarbon reactivity and nitrogen oxide levels in the exhaust which they attributed to differences in fuel density which affected the carburetor metering characteristics. They also found that fuel olefin content had no significant effect on reactivity or nitrogen oxides. They concluded that fuel composition had no significant effect on reactivity or nitrogen oxides. They concluded that fuel composition had no significant effects on exhaust emissions as measured over a driving cycle.

2.11.2 Fuel Additives

The use of fuel additives to clean engine parts and maintain emission control systems has received much public attention recently with the advertising campaigns for Standard of California's F-310 additive. This additive is known to be a polybutene amine and is classified as a detergent-dispersant additive (Kipp *et al.*, 1970). Another detergent-dispersant additive has been announced by Lubrizol Corp. (Sheahan *et al.*, 1969). The Lubrizol additive shows similar effects in removal of deposits from intake valves, but no data were reported on emissions effects. The paper by Kipp *et al.* describes the initial tests on the F-310 additive which

demonstrated its ability to make sharp reductions in emissions from very dirty cars. Subsequent to that a California Air Resources Board report showed that the additive had no significant effect on changing the emissions characteristics from cars in a "normal" vehicle population. Chevron Research Corp. has questioned the results of the state report and is currently running extensive tests on a fleet of cars to determine the effects of the additive on normal vehicle populations. Current indications from this ongoing test are that use of gasoline with this additive can bring about a 10-15% reduction in hydrocarbon and CO emissions from the average car.* This is attributed to the effect of the additive in maintaining cleanliness of the carburetor, intake system, and PCV valve.

2.11.3 Gaseous Fuels

The use of natural gas or liquid-petroleum gas has been shown to give reduced emissions. Baxter et al. (1968), compared emissions from unequipped vehicles, vehicles with 1968 controls and an LP-gas vehicle. They found the LPG vehicle to have lower emissions of all species except nitric oxide. Further, the reactivity of exhaust hydrocarbons from the LPG car was 70% below the gasoline exhaust. By fitting the LPG car with a catalytic muffler and running rich they were able to reduce the nitric oxide but increased the CO.

The use of natural gas was described in a recent news article (Chem. and Engr. News, 1970). Tests by the California State Air Resources Board on 19 natural gas vehicles showed average emissions of 2.1 grams per mile hydrocarbons, 7.5 grams per mile of CO and 1.9 grams per mile of NO. One vehicle in the test showed emissions of 0.98, 1.6, and 0.43 grams per mile of hydrocarbons, CO, and NO, respectively. In reporting the hydrocarbon figures the concentrations have been multiplied by 1/2 to take into account the reduced reactivity of hydrocarbon emissions from natural gas. The Air Resources Board also multiplies hydrocarbon emissions from LPG vehicles by 0.75 to account for the reduced reactivity of emissions from that fuel. The reactivity measurements are based on a subtractive column technique. The weighting factors used are 1 for paraffins, 3 for aromatics, and 8 for olefins (Chipman et al., 1968). The use of natural gas is appropriate for fleet operations where there is a central fueling station for all vehicles, but it would be difficult for general use because of the lack of a widespread distribution system. Nevertheless, its use in fleet vehicles can be an important factor in reduction of overall emissions since fleet operations account for 30% of vehicular fuel consumption in Los Angeles County, and similar figures can be

*Personal communication from E. E. Spittler, Chevron Research Corp.

expected in other metropolitan areas.

Ammonia has been proposed as a fuel. Various studies have been made on the operation of spark ignition, diesel, and gas turbine engines on ammonia. Obviously this fuel produces no hydrocarbons or carbon monoxide, but it produces as much or greater amounts of nitrogen oxides than hydrocarbon fuels. In addition, running at rich mixtures will produce some ammonia in the exhaust. Sawyer et al. (1968) discuss the production of nitrogen oxides from ammonia fuel and give references to other work with this fuel.

Another carbon-free fuel which has been proposed is hydrogen. Hoffman et al., (1969) have discussed the use of the reaction of hydrogen with magnesium-nickel and magnesium-copper alloys to produce metal hydrides that can be used for storage of the hydrogen. Again there is a question of the availability of the hydrogen supply.

Finally several people have proposed running engines on cryogenic oxygen instead of air. This would require some sort of exhaust recycle to provide the charge dilution to avoid excessive pressures in engines. Obviously the use of pure oxygen would eliminate oxides of nitrogen in the exhaust.

With the exception of gaseous fuels, the effects of fuel composition on emissions are small compared to engine effects. The use of natural gas fuel provides low emissions. If this were found to be a practical fuel, work would have to be done in maintaining distribution centers and assuring safe operation with this fuel. It would have to be used in liquified form to give vehicles sufficient range. The effect of gasoline composition is not so clear. Although various steady state tests indicate an effect from different fuel compounds it appears that normal vehicle operation as measured on a driving cycle shows little or no effect of fuel composition.

2.11.4 Lead - Its Effects on Emissions and Emission Control Systems

Any discussion of lead and its effects on vehicle emissions and emission control systems or devices must begin with a discussion of particulate matter in general. The "Morse Report" (U.S. Department of Commerce, 1967), reports that vehicles account for one million tons of particulates per year. In a statement by Diggs (1970) to the California Air Resources Board, it was stated that there is a need for a clear definition of the term "particulate matter." Furthermore, measuring and characterizing the particles in the exhaust and the techniques and hardware to make measurements are only now being developed. Diggs in his statement mentions a filter unit composed of a cylindrical drum packed with high

efficiency fiberglass filter media which can withstand exhaust temperatures and accommodate the total exhaust flow without affecting performance for use as a particulate collecting system. To determine the lead in the exhaust with this filter system, it is a simple matter to extract the lead and other iron particles with acid and then analyze for metal content. On the other hand, for total particulate emission rates, the weight of the filter is measured. Using this weight gain method, there were appreciable amounts of particulates with both leaded and unleaded fuel reported. Hirschler and Marsee (1970) reported that lead is responsible for one third or less of the particulate emissions, that only a portion of the lead burned in the fuel is exhausted, and the percentage of lead exhausted becomes less as the operating conditions become lighter. This reference as well as the Diggs statement describe particulate trapping systems which could be used to reduce particulate emissions. Briefly, these are inertial cyclone type devices which separate and retain the particulate matter and is attached to the exhaust system.

One question which is frequently asked is, what is the effect of lead on emissions other than particulate? Gagliardi in 1967 and Gagliardi and Ghannam in 1969 investigated this question using non-exhaust device engines placed in customer operation. The program was to determine the effect of several concentrations of tetraethyl lead (TEL) in the fuel on exhaust emissions, engine deposits and wear. After 18,000 miles of operation using TEL concentrations of 0.5, 1.5, and 3.0 ml/gallon, the exhaust hydrocarbon (HC) emissions were similar; however, the levels were at least 150 ppm above the levels obtained with unleaded fuel. Also, the major increase in HC levels were noticed within 3000 miles of operation. There were little or no effects on CO and NO emissions observed by using leaded versus unleaded fuel. Higher ring wear and blow-by rates were noted as the TEL concentration was increased. There were also no deleterious effects on engine components observed during tests. Finally, engine deposits increased with increases in TEL concentrations. Du Pont data (Pahnke and Conte, 1969) show only a small (ca. 7%) increase in exhaust hydrocarbons due to lead deposits.

The lack of effects on engine components as was mentioned is noteworthy since it has been shown that unleaded fuel can cause excessive wear and failure of exhaust valves and seats (Mobil Research and Development Corporation, 1970). This Mobil report states that the lead alkyls in gasolines form an ash deposit on the valve faces and seats which acts as a solid lubricant. Without the lead alkyls, such as in unleaded fuel, direct contact of the valve and seat permits severe wear. Excessive seat wear can result in burned exhaust valves due to the poor seal between the valve and seat, and a loss of engine power caused by the recession of the valve seat. Mobil suggests the use of small

lead concentrations, on the order of .5 gm/gallon, as a solution to the problem. The other solution would be to use high alloy valves and valve seat inserts and also control valve cooling, such as sodium cooled valves.

One of the main problems with having lead in the fuel is its effects on proposed emission control systems proposed for reducing emissions to meet future standards. The three most proposed systems are exhaust gas reactors, exhaust gas recirculation, and catalytic converters. "A Rational Program for Control of Lead in Motor Gasoline," a report by the Technical Advisory Committee to the California State Air Resources Board (1970) discusses the use of leaded fuel with these systems. Briefly, the lead and lead scavengers attack the metals and ceramics which are used for the exhaust reactors, although, Du Pont in the statment by Diggs (1970) claims to have developed reactors which are compatible with leaded fuels. Since the lead in the gasoline produces exhaust stream particulates, the design and construction of exhaust recirculation systems will be more complex and costly with leaded fuel. Finally, the lead rapidly deteriorates almost all known catalyst materials reported.

The report made by the Technical Advisory Committee to the California State Air Resources Board mentioned earlier included a recommendation for the reduction and eventual elimination of leaded gasolines in California. Basically it calls for a marked reduction in the allowable lead levels in gasolines commencing in 1971 with some lead free gasolines, and beginning in 1977 to have no fuel sold in California which contains lead.

That report points out that nearly 95% of the 1971 model year cars will be able to run with a low octane (91 Research Octane Number) gasoline. Consequently the recommendations for gradual removal of lead from gasoline are based on a continually increasing fraction of the vehicle population which is able to run on lower octane gasoline. Thus to meet the recommendation of no lead in gasoline by 1977 it will not be necessary to duplicate the current octane levels of gasoline. Because of this past cost estimates for production of lead-free fuels, which have been based on the assumption that current octane levels will be maintained, are no longer valid.

Workers at the Bureau of Mines (Dimitriades et al., 1970) have predicted that lead-free gasoline will give higher reactivity, as measured in their irradiation chamber experiments. This was true for both evaporative and exhaust hydrocarbon emissions. The change in reactivity as measured on other scales was not so large, however. Again, these comparisons are based on the assumption that octane number requirements will not be changed. The studies reported compared fuels of the same octane number with and

without lead. The increase in octane number in the clear fuels was obtained by the addition of aromatics. This increase in aromatic content of the gasoline as was given as the cause for the increased reactivity. No experiments were made on the comparison of reactivity from high octane leaded fuels with that from low octane nonleaded ones.

The question of lead removal from gasoline is currently under debate in both California and federal legislatures. The rationale for removal from lead is due primarily to its effects on emissions of hydrocarbons and the ability to use catalytic control devices if lead is removed. The possible health effects are generally considered to be a secondary reason for lead removal from gasoline.

Section 3

CURRENT DEVELOPMENTS

3.1 INTRODUCTION

Because of the early attention focused on the automobile, especially in California, extensive research programs on automotive air pollution have been set up in the past, are continuing now, and will be expanded in the future. Research organizations can be roughly divided into the following groups: 1) automotive, petroleum and related industries whose primary concern is in fulfilling immediate legislative requirements, but who are also concerned with long range implications; 2) governmental research projects which are primarily concerned with long range studies; this includes work done by government research labs and contract research done by outside organizations; and 3) universities and associated research labs who are concerned with basic research in pollutant formation processes; much of this work is funded by governmental research grants. Naturally there is some overlap in this classification scheme, but this will serve as a basis for the discussion below.

3.2 AUTOMOTIVE AND PETROLEUM COMPANY RESEARCH

Automotive and petroleum company research is carried out by individual companies and by joint research efforts. One example of a joint automotive/petroleum research is the Inter-Industry Emission Control (IIEC) program which was begun in 1967 by Ford and Mobil. Nine other companies (5 U. S. oil companies and 4 foreign automobile manufacturers) are now participating in this program. The IIEC established goals of 89% reduction of carbon monoxide, 94% reduction of hydrocarbons, and 89% reduction of nitrogen oxides, and is developing systems to meet these goals. They have developed road vehicles which can obtain these reductions, but such vehicles are prototypes and effort is now in progress to make these vehicles economical and dependable mass-production cars.

Another automotive/petroleum collaborative research effort is carried out by Chrysler and Esso. Some of the systems developed by this group have been described in the previous section. Again these systems represent prototypes on which further developmental work is required.

The Coordinating Research Council (CRC) has set up a large research program covering various aspects of air pollution. This

is a joint government/industry program involving the Automobile Manufacturers Association (AMA), the American Petroleum Institute (API), and the National Air Pollution Control Administration (NAPCA). The main purpose of this program is to develop basic information rather than specific hardware, but much of the program is devoted to finding basic information related to specific immediate problems. In addition to its participation in the CRC program, the API is also carrying out its own program of emissions research.

3.3 CURRENT FEDERAL RESEARCH

The National Air Pollution Control Administration is carrying out extensive research programs, aiming to fill gaps in research programs carried out by industrial organizations. This is done by work at their own facilities and by contracts with various industrial organizations. In addition, NAPCA administers research grants to non-profit organizations for basic studies. Spokesmen for the automobile industry have constantly said that they are willing to consider any power plant for automotive applications. Despite these statements there is a feeling outside of the automotive industry that the industry is not giving enough support to the development of alternative power systems. Consequently there seems to be a tendency for the governmental research projects to emphasize non-conventional engine developments.

3.4 PRIVATE INDUSTRY PROPOSED RESEARCH

In preparing to meet emissions standards for the next 5 years automotive, petroleum and related industries are investigating in great detail the use of catalytic and thermal afterburners, exhaust manifold reactors, exhaust gas recirculation, design modifications of engines, intake systems, carburetors, etc., evaporative control devices, and fuel composition. Diesel manufacturers have been primarily concerned with control of odor and smoke. They have also done some work in nitrogen oxides emissions. As standards for gasoline powered vehicles become more stringent the contribution of the Diesel to hydrocarbons and carbon monoxide emissions will become more important and is under investigation. There is not much information available in the open literature about the emissions from small engines (motorcycles, outboard motors, etc.). Manufacturers of such engines are considering redesign of the engine to reduce its emissions.

Automotive and petroleum companies also carry out basic research in areas such as combustion and battery systems. Batteries

such as sodium-sulfur, air-zinc, and lithium-chlorine are under consideration. The gas turbine is given major consideration as an alternative power plant. Although some work in external combustion engines (Rankine and Stirling cycles) has been carried out, these programs appear to be somewhat minimal.

Finally, these companies are also working in areas such as test procedures, instrumentation, production controls, and follow-up service. They also carry out various air pollution research programs on subjects such as atmospheric chemistry and health effects which are not directly related to automotive emissions control.

Turbojet engine manufacturers have been primarily concerned with the control of visible smoke from their engines. This has been done by combustor redesign. These companies are also conducting research into the formation of nitric oxide in turbine engines.

3.5 FUTURE GOVERNMENTAL RESEARCH PLANS

The NAPCA projects cover extensive areas of vehicle emissions. A report on current and proposed projects ("Federal Research and Development Plan for Mobile Sources Pollution Control") is to be issued in July or August, 1970. Current federally funded programs include the following specific topics: induction systems, carburetors, influence of fuel vaporization, nitric oxide kinetics, alternative fuels, effects of gasoline additives, control technique evaluation, exhaust gas recirculation, nitrogen oxides control, control of particulate emissions, effects of fuel composition and volatility, emissions due to vapor evolution and spillage while cars are being fueled, 2-cycle engine emissions, off-highway vehicle emissions, diesel emissions control, diesel smoke, and odor, aircraft emissions, Rankine cycle propulsion systems, continuous flow combustors for vehicle propulsion systems, measurements of oxygenates and particulates in vehicle exhausts, measurement of polynuclear aromatic hydrocarbons in exhausts, reactivity measurements, odor measurement and characterization, sampling system evaluation, and various programs in fundamental combustion research.

Other federal agencies are also doing work related to emissions. Some of this work is funded by transfers of funds from NAPCA. The Department of Defense is interested in developments in power plant design; some of their work is in engines which have potentially low emissions such as stratified charge engines, gas turbines, and electric cars. They are also doing some basic combustion research. The Bureau of Mines has been carrying out work

at their Bartlesville Petroleum Research Center on the relations between fuel composition and vehicle emissions. This includes studies on conventional spark ignition and diesel engines as well as aircraft engines. The Department of Transportation has sponsored programs in aircraft emissions and buses powered by external combustion engines and hybrid electric systems.

Ongoing and proposed research programs include controls of conventional vehicles by various techniques. These involve various systems in combination to simultaneously reduce all gaseous pollutants. Typical noncatalytic approaches involve exhaust gas recycle for NO control and some form of exhaust reactor. Catalytic systems include oxidizing catalysts, with NO control by other techniques, and dual catalyst systems for reduction of all three CO, NO, and hydrocarbons. The dual catalyst systems will either use a combination of reducing catalyst/intermediate air injection/oxidizing catalyst or the addition of a reactant such as ammonia which can reduce NO in an oxidizing atmosphere. Control of particulates by use of unleaded fuels and/or mechanical removal from exhaust gases will be examined. Evaporative emissions in both vehicle operation and refueling will be investigated and controls of these emissions will be developed.

Emissions from other conventional engines, such as 2-cycle engines, aircraft turbines, and diesels will also be explored. Many of the control techniques applied to 4-cycle engines can be applied to 2-cycle engines with suitable design modifications. The main thrust of the proposed research in diesel emissions will be in control of odor, smoke, and oxides of nitrogen. Work on aircraft emissions is aimed at reduction of particulate matter and oxides of nitrogen.

Work is planned on alternative power plants, both heat engines and electric systems. Rankine cycle, Stirling cycle, and gas turbine engines will be developed. The goals of the research programs for these three engine types are different. These goals are related to the current state of knowledge about such engines. Development of high temperature alkali-metal batteries and metal-air batteries will also be carried out. Finally various hybrid electric/heat engine power systems will be studied. No federal work appears to be planned on fuel cells for vehicular applications.

Section 4

BASIC AND APPLIED RESEARCH NEEDED

4.1 GENERAL NEEDS

Research is needed in the general area of emissions reduction for 1974 and later model year cars. The emissions standards for earlier years can be met by existing technology and the development of this technology for use in production vehicles is currently given great attention by the automobile manufacturers. Beginning with later model year cars, however, new advances in technology will be required to meet emissions standards. This may require the development of catalytic devices or alternative power plants.

The areas of vehicle emission from conventional engines about which there is still some uncertainty should be investigated. A major example of this is the production of oxygenated material in automobile exhaust. Finally, continuing basic research into engine combustion processes should be carried out; this research may lead to a better understanding of possible control methods for future low emission vehicles.

4.2 BASIC RESEARCH STUDIES

Basic research projects are required in the general areas of combustion, catalysis, and battery development. In each of these areas improvements in basic understanding could contribute to reduction of pollution. Combustion studies should be carried out not only in conventional spark ignition engines, but also in prototype combustors for other engines. Battery research should be aimed at development of the necessary high energy and power density batteries required for vehicular propulsion. In the area of catalysis it is necessary to find an effective catalyst for the removal of nitric oxide that is compatible with removal of hydrocarbons and CO. A better understanding of the fundamental processes involved in the catalytic NO reduction process would be of importance here.

4.3 APPLIED RESEARCH TASKS

One of the primary tasks here is the determination of the role that the oxygenated material in automobile exhaust plays in the photochemical smog process. This implies a joint study of

various task force groups including the instrumentation necessary for effective and routine determination of exhaust aldehydes, and the establishment of a reactivity measure for these compounds in terms of their effects on photochemical smog. If the current spark ignition engine is to remain as the primary power source for the next several years an accurate measure of the exhaust aldehydes is necessary to obtain a complete picture of its emissions.

Applied research is also needed in the design and development of catalytic control devices which are capable of long in-use service. Although there are already some catalysts available which can reduce emissions in laboratory situations, they encounter difficulties in vehicle service. These arise from poisoning (mainly from lead, but also from sulfur) and catalyst attrition. The primary cause of this attrition is probably engine vibration.

As automotive spark ignition engines come under increasingly stringent controls it will be necessary to consider controls on other engines which have been neglected in the past because of their small contribution to the overall pollution picture. The diesel engine and the aircraft gas turbine are the two largest minor sources which have not come under comprehensive controls. If the diesel engine is gradually replaced by gas turbines for heavy-duty applications, control of this engine may not be so important. If the diesel engine maintains a significant role in the transportation picture the first emissions which should come under control are odor, smoke, and nitrogen oxides. Similarly the main emissions problems from the aircraft gas turbine will be smoke and nitrogen oxides. The odor from these engines, which provides a local nuisance at airports, should also be investigated.

The gas turbine appears to be the most likely candidate as a replacement engine for conventional ground vehicle transportation. The major problem with application of this engine appears to be its nitric oxide emissions. Developmental work is also required to provide efficient operation of gas turbine engines in smaller sizes.

Other engines are still in an experimental state. Stirling and Rankine engines will require large amounts of development to be able to compete economically with conventional engines. It appears that emissions from these engines are already low; consequently, the major work needed in these engines is improvement of their other performance characteristics and reduction of their size, weight, and cost.

Development of electric vehicles will require basic work on battery systems. Conceptual design of such cars and their role in the overall transportation picture is about the only developmental task feasible at this time. It would also be interesting to

have a combined study with the task force investigating emissions from stationary sources to obtain an accurate picture of the real impact of electric vehicles on air pollution.

4.4 TRANSPORTATION

There appears to be little effort relating air pollution to the total problem of transportation and traffic. (As a personal opinion the city of San Francisco has a greater problem with traffic than it does with air pollution.-LSC) Some study should be given to the possible reduction of air pollution by increased use of mass transit or more efficient traffic patterns in existing urban areas.

Section 5

TASKS RECOMMENDED FOR PROJECT CLEAN AIR

5.1 GENERAL RATIONALE

It can be seen that there are many areas for possible research in motor vehicle emissions and control. There are also many research projects, continuing and proposed, by private industry and governmental agencies. Ideally the University should attempt to carry out research in those areas which are not currently under study, or which are receiving a minimal amount of attention. It would not seem appropriate, then, to consider development of control devices to be placed on cars in the next 1-3 years. The general target date for application of the results of the research programs then should be 1974-1975.

Another obvious constraint on the research projects of Project Clean Air is that they must rely on areas of current faculty interest. On the basis of proposals received by Project Clean Air prior to April 14, 1970, it is possible to divide faculty interest into 5 broad areas: Catalysis, Basic Combustion, Conventional Vehicle Development, Nonconventional Vehicles, and Battery Systems. (There is, of course, a final miscellaneous category.) Based on the review of the literature given in Section 2 and faculty interest as manifested in the proposals submitted, these are the subject areas recommended for research projects in Project Clean Air.

No real priorities are indicated by the listing of the subject areas. Any assignment of priorities will have to be done on the basis of individual projects. The following sections give a listing of interested faculty (in alphabetical order) for each subject area.

5.2 CATALYSIS

Interested faculty in this area are:

R. W. Anderson (Chemistry, Santa Cruz)

A. T. Bell (Chemical Engineering, Berkeley)

J. F. Bunnett (Chemistry, Santa Cruz)

C. Chu (Energy and Kinetics, Los Angeles)

V. E. Denny (Energy and Kinetics, Los Angeles)

A. F. Mills (Energy and Kinetics, Los Angeles)

Ken Nobe (Energy and Kinetics, Los Angeles)

R. L. Perrine (Energy and Kinetics, Los Angeles)

E. E. Petersen (Chemical Engineering, Berkeley)

R. G. Rinker (Chemical and Nuclear Engineering, Santa Barbara)

O. C. Sandall (Chemical and Nuclear Engineering, Santa Barbara)

Proposed research projects include studies of basic catalytic phenomena related to emissions chemistry, development of effective catalysts for control of pollutants, and design and development of catalytic reactors to be tested on actual vehicles.

5.3 BASIC COMBUSTION

Interested faculty in this area are:

R. W. Anderson (Chemistry, Santa Cruz)

J. F. Bunnett (Chemistry, Santa Cruz)

E. A. Grens II (Chemical Engineering, Berkeley)

O. T. Hanna (Chemical and Nuclear Engineering, Santa Barbara)

E. L. Knuth (Energy and Kinetics, Los Angeles)

A. F. Mills (Energy and Kinetics, Los Angeles)

R. G. Rinker (Chemical and Nuclear Engineering, Santa Barbara)

L. B. Robinson (Materials, Los Angeles)

R. F. Sawyer (Mechanical Engineering/Thermal Systems, Berkeley)

E. S. Starkman (Mechanical Engineering/Thermal Systems, Berkeley)

Proposed topics in this area include studies of basic combustion chemistry, combustion modeling in real combustors, droplet burning studies, and experiments on engines.

5.4 CONVENTIONAL VEHICLE DEVELOPMENT

Interested faculty in this area are:

D. O. Harris (Chemistry, Santa Barbara)

R. S. Hickman (Mechanical Engineering, Santa Barbara)

J. A. Howard (Electrical Engineering, Santa Barbara)

R. F. Sawyer (Mechanical Engineering/Thermal Systems, Berkeley)

E. R. Stevens (Air Pollution Research Center, Riverside)

E. S. Starkman (Mechanical Engineering/Thermal Systems, Berkeley)

Proposed projects include the establishment of a vehicle testing lab to perform experiments of various immediate problems of vehicle emissions as they arise, studies of aldehyde emissions from conventional vehicles, and a study of the use of cryogenic oxygen for elimination of nitrogen oxides.

5.5 NON-CONVENTIONAL VEHICLES

Interested faculty in this area are:

R. L. Burton (Aerospace and Mechanical Engineering Sciences, San Diego)

E. Marschall (Mechanical Engineering, Santa Barbara)

R. F. Sawyer (Mechanical Engineering/Thermal Systems, Berkeley)

E. S. Starkman (Mechanical Engineering/Thermal Systems, Berkeley)

W. T. Thompson (Mechanical Engineering, Santa Barbara)

R. C. Wood (Electrical Engineering, Santa Barbara)

Projects in this area include steam car development, design and testing of combustors for non-conventional engines, and construction of a hybrid heat engine/electric vehicle.

5.6 BATTERY DEVELOPMENT

Interested faculty in this area are:

D. N. Bennion (Energy and Kinetics, Los Angeles)

J. H. Kennedy (Chemistry, Santa Barbara)

Studies with both liquid and solid electrolytes have been proposed.

5.7 MISCELLANEOUS

The following proposals do not fit into the classification scheme given above:

G. R. Heidbreder (Electrical Engineering, Santa Barbara)
Municipal Traffic Control and Communication Systems

O. T. Hanna and O. C. Sandall (Chemical and Nuclear Engineering, Santa Barbara)
Dispersion of Pollutants Emanating from Jet Aircraft Exhaust

P. F. Ordung (Electrical Engineering, Santa Barbara)
Determination of Pollution Emission From Individual Vehicles on Highways

The last two proposals appear to fall in the realm of other task forces (atmospheric modeling and instrumentation, respectively).

Section 6

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